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2D hydrogen bond networks in the crystals of [(NH$_4$ · H$_2$O)$_2$][(RO)(Fc)P(S)$_2$]$_2$ (R = 3-(BzO)-Bz, 4-(*n*-Bu)-Bz, Bz = benzyl)

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Dedicated to Prof. Ionel Haiduc on the occasion of his 70th birthday.

Abstract

Herein we report on the preparation of hydrated ammonium salts of the dithiophosphonic acids (RO)(Fc)P(S)(SH) (R = derivative of benzyl) featuring [(NH$_4$ · H$_2$O)$_2$]$^{2+}$ cations formed by N–H···O hydrogen bonds. Interaction of these cations with the PS$_2$$^-$ units gives rise to unprecedented 2D networks, formed solely by hydrogen bonds. These unique networks containing two- and three centered hydrogen bonds are valuable examples of the acceptor properties of sulfur atoms.
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1. Introduction

The concept of Nebenvalenz published in 1902 by Werner [1], and the term "Hydrogen bridge atoms" used by Atsbury in 1933 [2] were one of the first stones in the description of the phenomenon defined later as a Hydrogen Bridge or a Hydrogen Bond. Nonetheless, it was Pauling who first introduced in 1939 the concept of hydrogen bond as an important principle in structural chemistry in *The Nature of Chemical bond* [3]. Currently, its importance has been well documented by the over 355,000 references in the chemical abstracts and by numerous monographs [4]. Moreover, many papers describing unusual 1D, 2D or 3D water chains, sheets or clusters, respectively, formed by hydrogen bonds have been reported [5]. Although, there

are not many reports on the acceptor properties of sulfur atoms, the hydrogen bonds dealing with sulfur as the acceptor atom have proven to be determinant in the tuning of the reactivity of the Zn···cystein thiolate moiety and the Fe–S clusters in proteins [6,7].

In our group, there is a long history in the chemistry of phosphorus-chalcogen moieties containing ligands as HN(PR$_2$E)$_2$ or HN(PR$_2$E)(PR$'_2$E) (E = O, S, Se and their combination, R, R$'$ = alkyl, aryl, alkoxyl), (RO)$_2$P(S)(SH) (R = alkyl, aryl) and their main-group elements derivatives [8]. Recently, we have focused our research on investigating the influence of the R group in tellurium complexes of the [(RO)(Fc)P(S)$_2$]$^-$ (R = benzyl derivative) anion on the resulting geometry. We decided to use the method of Fackler for the preparation of ferrocene bearing ligands [9], although several other preparations have been published [10], as the resulting ammonium salts were reported to be stable. During the isolation of the ammonium salts [NH$_4$][(RO)(Fc)P(S)$_2$] (R = 3-(BzO)-Bz (**1a**), 4-(*n*-Bu)-Bz (**2a**), Bz = benzyl) we observed inclusion of water into the

samples and the formation of hydrated salts [(NH$_4$ · H$_2$O)$_2$][(RO)(Fc)P(S)$_2$]$_2$ (R = 3-(BzO)-Bz (**1**), 4-(*n*-Bu)-Bz (**2**), Bz = benzyl). Compounds **1** and **2** contain unusual examples of 2D networks formed solely by hydrogen bonds and involving the rare [(NH$_4$ · H$_2$O)$_2$]$^{2+}$ cation.

2. Experimental

2.1. Materials

Gaseous ammonia was purchased from Praxair and dried by passing through a column filled with sodium wire. All solvents were dried prior to use.

2.2. Physical measurements

Infrared spectra were recorded as CsI powders in the range 4000–250 cm^{-1} on a Bruker Tensor 27 Fourier-transform spectrometer using the method of diffused reflectance; ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded using a JEOL ECLIPSE 300 NMR spectrometer. Mass spectra (ESI-ITMS) were recorded using a Bruker Daltonics Esquive 6000 spectrometer. Elemental analyses (C, H, N) were carried out by Galbraith Laboratories Inc. (Knoxville, TN).

2.3. Preparation of compounds

The preparation of the anhydrous salts **1a** and **2a** were performed in a dry and oxygen-free atmosphere (N$_2$ or Ar) by using Schlenk-line and glove-box techniques. Ferrocenyl Lawesson's Reagent [11] (FcLR) was prepared using the literature procedures.

2.3.1. Synthesis of [NH$_4$][(3-(BzO)-BzO)(Fc)P(S)$_2$] (1a)

A mixture of FcLR (1.00 g, 1.78 mmol) and 3-benzyloxybenzyl alcohol (0.76 g, 3.56 mmol) in benzene (40 mL) was refluxed for 3 h. The resulting brown-orange solution was placed in an ice bath, and the mixture stirred for 30 min. Anhydrous gaseous NH$_3$ was slowly bubbled through the solution at 0 °C for 1 h. The color of the solution changed from orange to dark brown and a small amount of insoluble material precipitated out. The reaction mixture was filtrated and all volatiles were removed under vacuum. The crude product was recrystallized from a CH$_2$Cl$_2$/hexane mixture to yield **1** as a pale yellow powder. Yield: 1.42 g (78%); m.p. 116–118 °C; Elemental analysis (%) calcd. for C$_{24}$H$_{26}$FeNO$_2$PS$_2$ (511.42): C 56.37, H 5.12, N 2.74; found: C 56.62, H 5.20, N 2.81%; IR (CsI): ṽ 2905 (vs br, vNH + vCH), 1598 (s, δ NH$_4^+$), 1444 (s, vP–C), 1272 (s, vP–O–C), 1046 (m, vP–O–C), 824 (m, δ CH$_2$), 672 (vs, v_{asym}P–S), 584 cm^{-1} (s, v_{sym}P–S). ^{1}H NMR ((CDCl$_3$/DMSO-d_6), 20 °C, TMS): δ = 4.26 (s, 5H, *H* of Cp), 4.32 (bs, 2H, *H* of Cp), 4.60 (bs, 2H, *H* of Cp), 4.90 (d, ^3J(H,P) = 8.3 Hz, 2H, C*H$_2$*–O), 5.01 (s, 2H, Ar–C*H$_2$*–O–Ar), 6.76 (br s, 4H, N*H$_4^+$*), 6.86–7.43 ppm (m, 9H, *H* of Ar); ^{13}C NMR ((CDCl$_3$/DMSO-d_6), 20 °C,

TMS): δ = 66.4 (*C*H$_2$–O), 70.1 (Ar–*C*H$_2$–O–Ar), 70.5 (*C* of Cp unsubst.), 70.8, 70.9 (*C* of Cp subst.), 71.6 (d, ^1J(C,P) = 16 Hz, *C* of Cp subst.), 114.5, 114.8, 120.7, 127.8, 128.1, 128.7, 129.9, 136.9, 139.5, 158.9 ppm (*C* of Ar); ^{31}P{^{1}H} NMR ((CDCl$_3$/DMSO-d_6), 20 °C, 85% H$_3$PO$_4$): δ = 107.4 ppm. Mass Spec (ESI-ITMS): *m/z* 493 [M−NH$_4$]$^-$.

2.3.2. Synthesis of [(NH$_4$ · H$_2$O)$_2$][(3-(BzO)-BzO)(Fc)P(S)$_2$]$_2$ (1)

1a (1.00 g, 1.96 mmol) was dissolved in wet THF (30 mL) and stirred for 10 min. All the volatiles were removed under vacuum to give **1** as a brown-orange microcrystalline material in a quantitative yield (1.04 g, 100%); m.p. 154–155 °C. Elemental analysis (%) calcd. for C$_{24}$H$_{28}$FeNO$_3$PS$_2$ (529.43): C 54.45, H 5.33, N 2.65; found: C 54.12, H 5.42, N 2.55%; IR (CsI): ṽ 3393 (m br, v H$_2$O), 3261 (s br, vH$_2$O), 2941 (vs br, vNH + vCH), 1598 (s, δ NH$_4^+$), 1444 (s, vP–C), 1175 (s, vP–O–C), 1013 (vs, vP–O–C), 823 (vs, δ CH$_2$), 651 (s, v_{asym}P–S), 586 cm^{-1} (s, v_{sym}P–S). ^{1}H NMR ((CDCl$_3$/DMSO-d_6), 20 °C, TMS): δ = 1.32 (br s, 4 + 2H, N*H$_4^+$* and *H$_2$O*), 4.20 (bs, 5 + 2H, *H* of Cp unsubst. + subst.), 4.61 (bs, 2H, *H* of Cp subst.), 4.87 (d, 2H, ^3J(H,P) = 8.5 Hz, C*H$_2$*–O), 4.96 (s, 2H, Ar–C*H$_2$*–O–Ar), 6.75–7.37 ppm (m, 9H, *H* of Ar); ^{13}C NMR ((CDCl$_3$/DMSO-d_6), 20 °C, TMS): δ = 65.8 (s, *C*H$_2$–O), 70.0 (s, Ar–*C*H$_2$–O–Ar), 70.4 (*C* of Cp unsubst.), 70.4, 70.4 (*C* of Cp subst.), 71.7 (d, ^1J(C,P) = 14 Hz, *C* of Cp subst.), 114.2, 114.2, 120.5, 127.7, 127.9, 128.6, 129.4, 137.1, 140.1, 158.8 ppm (*H* of Ar); ^{31}P{^{1}H} NMR ((CDCl$_3$/DMSO-d_6), 20 °C, H$_3$PO$_4$): δ = 108.4 ppm.

2.3.3. Synthesis of [NH$_4$][(4-(n-Bu)-BzO)(Fc)P(S)$_2$] (2a)

A mixture of FcLR (0.85 g, 1.52 mmol) and 4-*n*-butylbenzyl alcohol (0.50 g, 3.04 mmol) in benzene (40 mL) was refluxed for 3 h. The resulting brown-orange solution was placed in an ice bath, and stirred for 30 min. Anhydrous gaseous NH$_3$ was slowly bubbled through the solution at 0 °C for 1 h. The color of the solution changed from brown-orange to dark green and a small amount of insoluble material precipitated out. The reaction mixture was filtrated and all volatiles were removed under vacuum. The crude product was recrystallized from CH$_2$Cl$_2$/hexane mixture to yield **2a** as a pale green yellow powder. Yield: 0.79 g (56%); m.p. 114–116 °C. Elemental analysis (%) calcd. for C$_{21}$H$_{28}$FeNOPS$_2$ (461.40): C 54.67, H 6.12, N 3.04; found: C 54.32, H 6.05, N 3.10%; IR (CsI): ṽ 2955 (vs br, vNH + vCH), 1514 (m, δ NH$_4^+$), 1406 (s, vP–C), 1171 (m, vP–O–C), 986 (s, vP–O–C), 822 (s, δ CH$_2$), 675 (s, v_{asym}P–S), 579 cm^{-1} (s, v_{sym}P–S). ^{1}H NMR (CDCl$_3$, 20 °C, TMS): δ = 0.91 (t, 3H, ^3J(H,H) = 7.6 Hz, CH$_2$–C*H$_3$*), 1.33 (sext, 2H, ^3J(H,H) = 7.6 Hz, CH$_2$–C*H$_2$*–CH$_3$), 1.57 (q, 2H, ^3J(H,H) = 7.6 Hz, C*H$_2$*–CH$_2$–CH$_3$), 2.57 (t, 2H, ^3J(H,H) = 7.6 Hz, CH$_2$–C*H$_2$*–Ar), 4.26 (s, 5H, *H* of Cp unsubst.), 4.30 (bs, 2H, *H* of Cp subst.), 4.58 (bs, 2H, *H* of Cp subst.), 4.93 (d, 2H, ^3J(H,P) = 8.6 Hz, C*H$_2$*–O),

6.81 (bs, 4H, NH_4^+), 7.13–7.28 ppm (4H, H of Ar); ^{13}C (CDCl$_3$, 20 °C, TMS): $\delta = 14.1$ (CH$_2$–CH_3), 22.5 (CH_2–CH$_3$), 33.7 (CH_2–CH$_2$–CH$_3$), 35.5 (CH_2–Ar), 66.3 (CH_2–O), 70.5 (C of Cp unsubst.), 70.7, 70.8 (C of Cp subst.), 71.5 (d, ^1J(C,P) = 15 Hz, C of Cp subst.), 128.3, 128.8, 135.0, 142.9 ppm (C of Ar); ^{31}P{^{1}H} NMR (CDCl$_3$, 20 °C, H$_3$PO$_4$): $\delta = 106.5$ ppm. Mass Spec (ESI-ITMS): m/z 443 [M−NH$_4$]$^-$.

2.3.4. Synthesis of [(NH$_4$ · H$_2$O)$_2$][(4-(n-Bu)-BzO) (Fc)P(S)$_2$]$_2$ (2)

2a (1.00 g, 2.17 mmol) was dissolved in wet THF (30 mL) and stirred for 10 min. All the volatiles were removed under vacuum to give **1** as a brown-orange microcrystalline material in a quantitative yield (1.04 g, 100%); m.p. 74–76 °C. Elemental analysis (%) calcd. for C$_{21}$H$_{30}$FeNO$_2$PS$_2$ (479.40): C 52.61, H 6.31, N 2.92; found: C 51.45, H 6.12, N 2.83%; IR (CsI): $\tilde{v}$ 3385 (vs br, vH$_2$O), 2957 (vs br, vNH + vCH), 1514 (m, δ NH$_4^+$), 1416 (s, vP–C), 1177 (m, vP–O–C), 1009 (m, vP–O–C), 821 (m, δ CH$_2$), 652 (s, v_{asym}P–S), 484 cm^{-1} (m, v_{sym}P–S). ^{1}H NMR ((CDCl$_3$), 20 °C, TMS): $\delta = 0.81$ (t, 3H, ^3J(H,H) = 7.4 Hz, CH$_2$–CH_3), 1.23 (sext., 2H, ^3J(H,H) = 7.4 Hz, CH_2–CH$_3$), 1.46 (q, 2H, ^3J(H,H) = 7.4 Hz, CH$_2$–CH_2–CH$_3$), 2.40 (s, 4 + 2H, NH_4^+ and H_2O), 2.49 (t, 2H, ^3J(H,H) = 7.4 Hz, CH$_2$–CH_2–Ar), 4.17 (dd, 2H, ^3J(H,H) = 3.9 Hz, ^3J(H,H) = 4.1 Hz, H of Cp subst.), 4.20 (s, 5H, H of Cp unsubst.), 4.58 (s, 2H, ^3J(H,H) = 3.9 Hz, ^3J(H,H) = 4.1 Hz, H of Cp subst.), 4.84 (d, 2H, ^3J(H,P) = 8.3 Hz, CH_2–O), 7.00–7.20 ppm (m, 4H, H of Ar); ^{13}C (CDCl$_3$, 20 °C, TMS): $\delta = 14.0$ (CH$_2$–CH_3), 22.5 (CH_2–CH$_3$), 33.7 (CH_2–CH$_2$–CH$_3$), 35.5 (CH$_2$–CH$_2$–Ar), 66.4 (s, CH$_2$–O), 70.5 (C of Cp unsubst.), 70.5, 70.8 (C of Cp subst.), 71.6 (d, ^1J(C,P) = 14 Hz, C of Cp subst.), 128.3, 128.7, 135.0, 142.8 ppm (C of Ar); ^{31}P{^{1}H} NMR (CDCl$_3$, 20 °C, TMS): $\delta = 106.8$ ppm.

2.4. X-ray data collection and structure solution and refinement

Orange block-shaped single crystals of compounds **1** and **2** were obtained by slow evaporation of their saturated solutions in wet THF. A suitable crystal of each compound was covered with paraffin oil, mounted on a nylon loop, and placed immediately to the cold nitrogen stream (173 K). Diffraction data for **1** and **2** were collected on a Bruker three-circle diffractometer equipped with an APEX CCD area-detector using graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). Structures were solved by direct methods (SHELXS-97) [12] and refined by full-matrix least-squares methods on F^2 with SHELXL-97 [13]. The non-hydrogen atoms were refined anisotropically; hydrogen atoms were included at geometrically idealized positions and refined with the riding model except those attached to nitrogen and oxygen, which were localized from the electron density map and refined with distance restrains with U_{ij} set to 1.5 times the U_{ij} of the parent atom. Crystal data

and refinement details for compounds **1** and **2** are presented in Table 1. Selected bond lengths and angles for **1** and **2** are given in Table 2.

Table 1
Crystallographic data for the structural analyses of compounds **1** and **2**

	1	**2**
Empirical formula	C$_{24}$H$_{28}$FeNO$_3$PS$_2$	C$_{21}$H$_{30}$FeNO$_2$PS$_2$
Formula weight	529.41	479.40
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
Temperature, K	173(2)	173(2)
Wavelength, Å	0.71073	0.71073
a, Å	21.754(4)	9.426(2)
b, Å	9.316(2)	11.747(3)
c, Å	12.445(3)	21.338(4)
α, °	90	74.19(3)
β, °	104.78(3)	82.79(3)
γ, °	90	89.05(3)
Volume, Å^3	2439(1)	2255(1)
Z	4	4
Density$_{calc}$, g cm^{-3}	1.442	1.412
Absorption coefficient, mm^{-1}	0.882	0.942
$F(000)$	1104	1008
Crystal size, mm^3	0.25 × 0.21 × 0.08	0.49 × 0.28 × 0.28
θ Range for data collection, °	2.39–25.35	1.80–25.06
Index ranges	−25 ⩽ h ⩽ 26	−11 ⩽ h ⩽ 11
	−11 ⩽ k ⩽ 11	−13 ⩽ k ⩽ 13
	−14 ⩽ l ⩽ 5	−25 ⩽ l ⩽ 25
Reflections collected	9804	24457
Independent reflections (R_{int})	4320 (0.0396)	7940 (0.0346)
Data/restraints/parameters	4320/7/307	7940/34/543
Goodness-on-fit on F^2	1.019	1.034
R_1,[a] $wR2$[b] ($I > 2\sigma(I)$)	0.0420, 0.0917	0.0348, 0.0826
R_1,[a] $wR2$[b] (all data)	0.0559, 0.0984	0.0415, 0.0863
Largest difference in peak/hole, e Å^{-3}	0.406/−0.254	0.525/−0.201

[a] $R = \sum ||F_o| - |F_c||/\sum |F_o|$.
[b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

Table 2
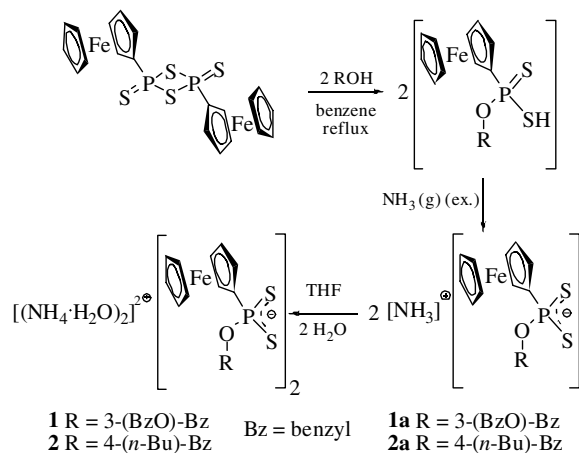Selected bond lengths [Å] and angles [°] of **1** and **2**

Compound **1**			
P(1)–S(1)	2.013(1)	S(1)–P(1)–O(2)	108.8(1)
P(1)–S(2)	1.968(1)	S(2)–P(1)–O(2)	111.9(1)
P(1)–O(2)	1.606(2)	S(1)–P(1)–C(15)	108.0(1)
P1(1)–C(15)	1.782(2)	S(2)–P(1)–C(15)	113.6(1)
S(1)–P(1)–S(2)	114.5(1)	O(2)–P(1)–C(15)	98.9(1)
Compound **2**			
Molecule 1			
P(1)–S(1)	2.012(1)	S(1)–P(1)–O(3)	108.7(1)
P(1)–S(2)	1.971(1)	S(2)–P(1)–O(3)	111.6(1)
P(1)–O(3)	1.607(2)	S(1)–P(1)–C(12)	108.5(1)
P1(1)–C(12)	1.783(2)	S(2)–P(1)–C(12)	113.2(1)
S(1)–P(1)–S(2)	114.6(1)	O(3)–P(1)–C(12)	99.1(1)
Molecule 2			
P(2)–S(3)	2.012(1)	S(3)–P(2)–O(4)	108.6(1)
P(2)–S(4)	1.968(1)	S(4)–P(2)–O(4)	111.8(1)
P(2)–O(4)	1.608(2)	S(3)–P(2)–C(33)	108.1(1)
P(2)–C(33)	1.786(2)	S(4)–P(2)–C(33)	113.1(1)
S(3)–P(2)–S(4)	114.8(1)	O(4)–P(2)–C(33)	99.4(1)

3. Results and discussion

Compounds **1a** and **2a** were prepared according the method of Fackler [9]. The equimolar amounts of the appropriate benzylic alcohol were refluxed with the Ferrocenyl Lawesson's Reagent FcP(S)(μ-S)$_2$P(S)Fc [11] (FcLR) (Fc = ferrocenyl) in benzene for 3 h. The solution was then placed in an ice bath for 30 min to cool to 0 °C and dry gaseous ammonia was bubbled through during one hour at this temperature. Filtration of the resulting suspension followed by the evaporation of all volatiles under vacuum and recrystallization of the crude product from a CH$_2$Cl$_2$/hexane mixture, afforded the products [NH$_4$][(RO)(Fc)P(S)$_2$] (R = 3-(BzO)-Bz (**1a**); R = 4-(*n*-Bu)-Bz (**2a**); Bz = benzyl) in moderate yields. Recrystallization of **1a** and **2a** from wet THF resulted in a formation of microcrystalline materials identified as [(NH$_4$ · H$_2$O)$_2$][(R-O)(Fc)P(S)$_2$]$_2$ (R = 3-(BzO)-Bz (**1**); R = 4-(*n*-Bu)-Bz (**2**)) by means of IR, ESI-MS (negative ions), multinuclear NMR techniques and unambiguously by X-ray structural analysis. Scheme 1 summarizes the preparation of compounds **1a**, **1**, **2a** and **2**.

3.1. ^1H and ^{31}P NMR and IR studies

The inclusion of water had only a small effect on the ^{31}P NMR spectra (δ 107.4 (**1a**), 108.4 (**1**), 106.5 (**2a**), 106.8 ppm (**2**)), but had a great effect on the position of the ^1H NMR signal for the NH$_4^+$ protons. Thus, the peak can be found at δ 6.76 ppm for **1a** as a broad singlet, whereas the inclusion of water causes this peak to move upfield to δ 1.32 ppm (includes now also the protons from water) in case of **1**. The situation is similar for **2a** and **2** and the signals can be found at δ 6.81 and 2.4 ppm (includes now also the protons from water). The difference between the chemical shift in **1** and **2** is most probably caused by the presence of DMSO-d_6 used to support the solubilization of **1** in the NMR sample. The inclusion of water can be further evidenced by the IR spectroscopy – water absorption bands at $\tilde{\nu}$ 3393, 3261 for **1** and 3385 cm^{-1} for **2** – whose broad character suggests presence of hydrogen bonding.

3.2. Structure of complexes 1 and 2

Compound **1** crystallizes in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit, whereas compound **2** crystallizes in a triclinic space group $P\bar{1}$ with two independent molecules in the asymmetric unit. Their crystal structures are shown in Fig. 1 (compound **1**) and Fig. 2 (compound **2**).

The X-ray structural analysis revealed the presence of an unusual centrosymmetric cation [(NH$_4$ · H$_2$O)$_2$]$^{2+}$ formed by four hydrogen bonds between the N–H protons from the ammonium ions and the oxygen atoms of the water molecules in both complexes **1** and **2**, respectively. The pro-
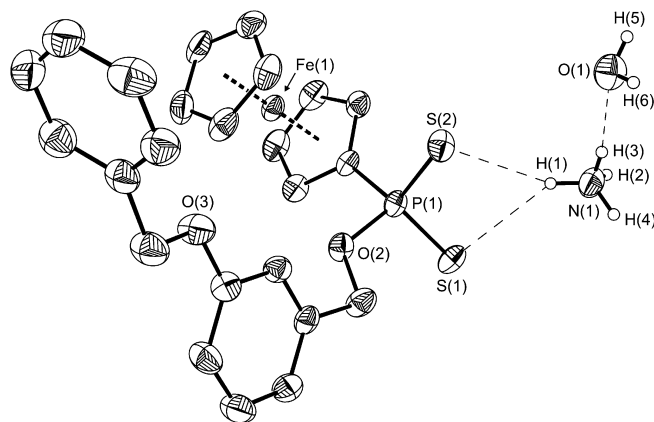

Fig. 1. Thermal ellipsoid plot of **1** at 50% level. Carbon-bound hydrogen atoms are omitted for clarity.
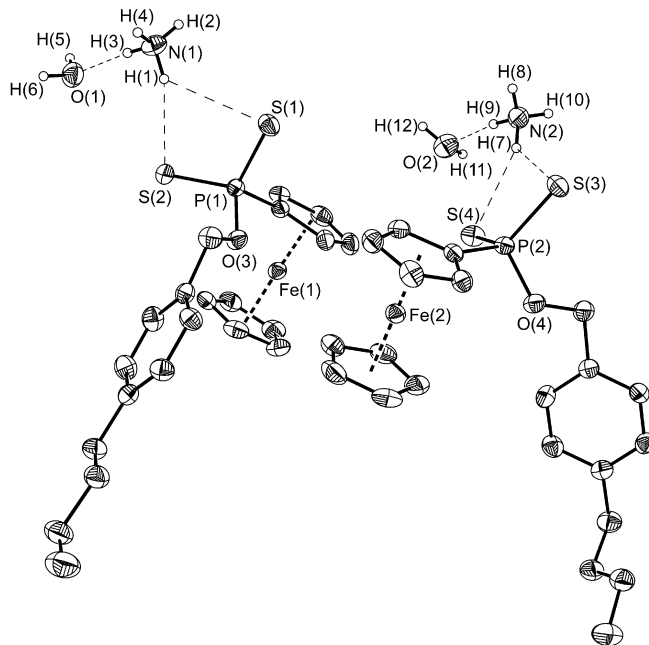

Fig. 2. Thermal ellipsoid plot of **2** at 50% level. Carbon-bound hydrogen atoms are omitted for clarity.

Scheme 1. Preparation of **1a**, **1**, **2a**, **2**.

found search in the CSD database gave to our surprise only 18 examples of such cation [14a]. Only in three cases, the cation is not localized on any symmetry element, as was also found in **2** [14b]. Moreover, these cyclic cations are in **1** and **2** bridged by the $[(RO)(Fc)P(S)_2]^-$ units into unprecedented 2D networks formed strictly by N–H⋯O, N–H⋯S or O–H⋯S two or three centered hydrogen bonds (Fig. 3) [15]. These 2D networks are localized in the (1 0 0) plane in the crystal of **1**, or in the (0 0 1) plane in case of **2**, respectively, while the organic residues and ferrocenyl moieties are in both cases filling the cell. This behavior can be compared to the hydrophobic and hydrophilic attractions present in cell membranes in biological systems.

There are numerous publications and reviews about hydrogen bonding in proteins, where the acceptor atom is either oxygen or nitrogen [4], but the publications corresponding to hydrogen bonding – where the acceptor atom is sulfur – are relatively scarce [6,7,16]. Therefore the definition regarding the distance between the hydrogen and sulfur atom which can be still considered as a part of the

A–H⋯S (A = O, N) hydrogen bond is not clear. The Jeffrey criterion for hydrogen bond used also by the International Union of Crystallography [17] defines the largest distance between the hydrogen and the acceptor atoms as $vdWR(H) + vdWR(A) - 0.12$ Å (vdWR = van der Waals Radii; which would be 2.60 Å for H⋯O, 2.63 Å for H⋯N and 2.88 Å for H⋯S, respectively, for these hydrogen – acceptor pairs), but longer distances are commonly accepted for asymmetric three centered hydrogen bonds occurring in proteins. The major components for such bonds have the O⋯H bond lengths from 1.6 to 2.9 Å (peak at 2.1 Å) with angles 90 to 175°, whereas the minor components have bond lengths from 2.05 to 3.0 Å (peak at 2.8 Å) with angles 90–175° [18]. Thus, taking into account the difference in vdW radii of oxygen (1.62 Å) and sulfur (1.80 Å) [19] – for a sulfur atom involved in an asymmetric three centered hydrogen bond – the distance to the hydrogen could be up to 3.18 Å. One can argue, that the basicity of the sulfur atom is lower than that of oxygen [20], but the fact, that the P–S bond lengths in **1** and **2** are very similar (2.013(1) and 1.969(1) for **1** and 2.012(1), 1.971(1), 2.012(1)
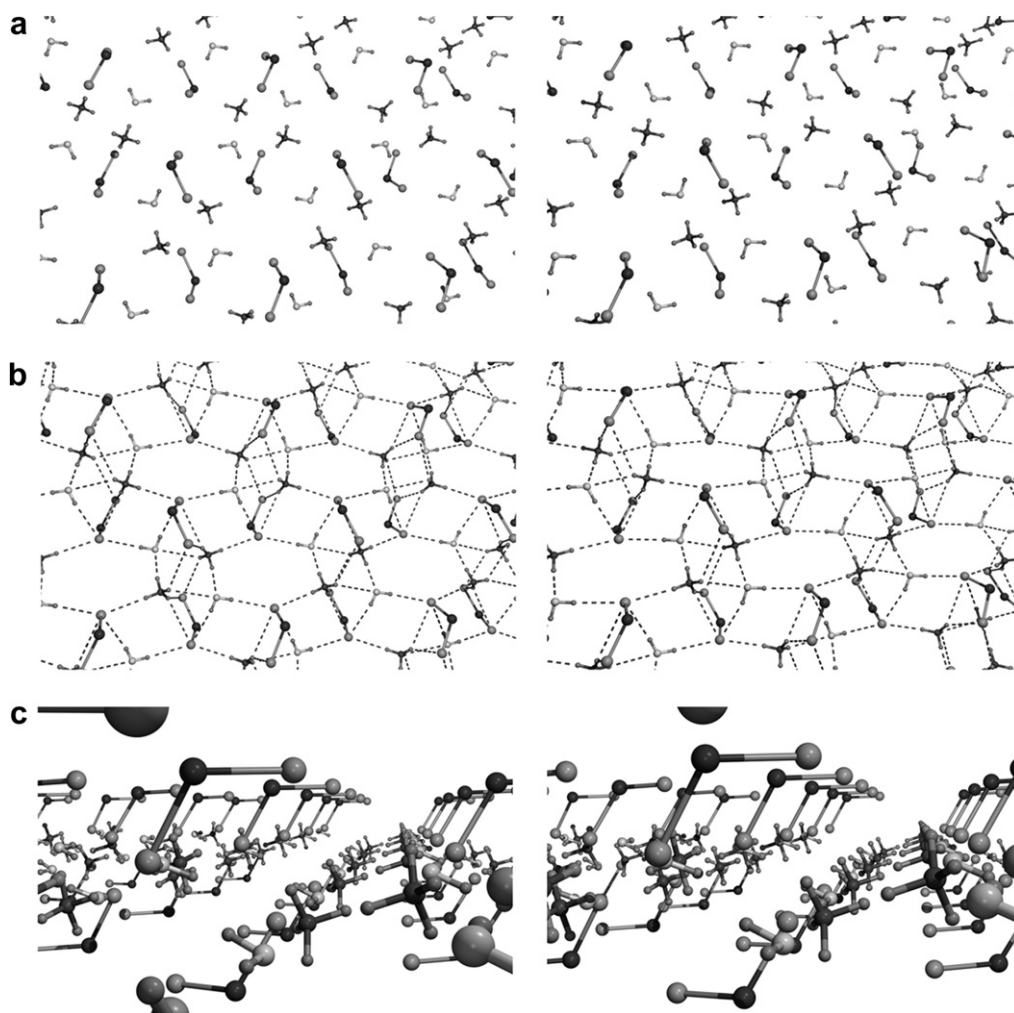

Fig. 3. First column: compound **1**, second column: compound **2**. View along the *a* cell axis in the crystal of **1**, along *c* axis in the crystal of **2**, respectively, without (a) and with (b) hydrogen bonds. View along the *b* cell axis in the crystal of **1**, along *a* axis in the crystal of **2**, respectively (c). All organic residues have been omitted for clarity.

Table 3
Bond lengths [Å] and angles [°] for the hydrogen bonds in **1** and **2**

D–H⋯A	d D–H	d H⋯A	d D⋯A	∠DHA
Compound 1				
N(1)–H(1)⋯S(1)#1	0.85(2)	3.00(3)	3.618(3)	131(3)
N(1)–H(1)⋯S(2)#1	0.85(2)	2.53(2)	3.325(3)	155(3)
N(1)–H(2)⋯S(2)#2	0.85(2)	2.94(3)	3.568(3)	132(3)
N(1)–H(2)⋯O(1)#3	0.85(2)	2.68(3)	3.089(4)	111(3)
N(1)–H(3)⋯O(1)	0.85(2)	1.97(2)	2.809(4)	170(3)
N(1)–H(4)⋯S(1)#3	0.86(2)	2.43(2)	3.279(3)	169(3)
O(1)–H(5)⋯S(1)#2	0.81(3)	2.49(3)	3.284(3)	170(4)
O(1)–H(6)⋯S(1)#4	0.83(3)	2.47(3)	3.297(2)	176(4)
Compound 2				
Molecule 1				
N(1)–H(1)⋯S(1)#1	0.88(1)	3.03(2)	3.659(3)	130(2)
N(1)–H(1)⋯S(2)#1	0.88(1)	2.49(2)	3.300(2)	153(2)
N(1)–H(2)⋯S(2)#2	0.88(1)	3.01(3)	3.572(3)	124(2)
N(1)–H(2)⋯O(1)#3	0.88(1)	2.49(3)	3.060(3)	123(2)
N(1)–H(3)⋯O(1)	0.89(1)	1.92(1)	2.809(3)	175(3)
N(1)–H(4)⋯S(3)#4	0.88(1)	2.42(1)	3.291(2)	170(3)
O(1)–H(5)⋯S(1)#2	0.87(2)	2.41(2)	3.277(2)	176(3)
O(1)–H(6)⋯S(3)	0.87(2)	2.48(2)	3.300(2)	172(3)
Molecule 2				
N(2)–H(7)⋯S(3)	0.89(1)	2.95(2)	3.610(3)	133(2)
N(2)–H(7)⋯S(4)	0.89(1)	2.51(2)	3.314(4)	151(2)
N(2)–H(8)⋯S(4)#2	0.88(1)	2.98(2)	3.559(3)	125(2)
N(2)–H(8)⋯O(2)#2	0.88(1)	2.54(3)	3.028(3)	115(2)
N(2)–H(9)⋯O(2)	0.89(1)	1.93(1)	2.815(3)	172(3)
N(2)–H(10)⋯S(1)#2	0.89(1)	2.43(1)	3.298(2)	165(3)
O(2)–H(11)⋯S(1)#5	0.88(2)	2.42(2)	3.297(2)	174(3)
O(2)–H(12)⋯S(3)#2	0.87(2)	2.44(2)	3.294(2)	166(3)

Symmetry transformations used to generate equivalent atoms for compound **1**: #1 $x, y - 1, z$; #2 $-x, -y + 1, -z + 1$; #3 $-x, y - 1/2, -z + 3/2$; #4 $x, -y + 3/2, z - 1/2$; Symmetry transformations used to generate equivalent atoms for compound **2**: #1 $-x + 1, -y + 1, -z$; #2 $-x + 1, -y, -z$; #3 $x - 1, y, z$; #4 $x - 1, y - 1, z$; #5 $-x, -y, -z$.

and 1.968(1) in **2**) compared to the theoretical values for a single (2.09 Å) [21] and double (1.86 Å) [22] phosphorus sulfur bond – suggests the occurrence of delocalization of the negative charge between both sulfur atoms of the PS_2 unit, thus enhancing their basicity. Although the cell parameters and the anions for **1** and **2** are different, the connectivity of the atoms in the 2D network is in both compounds very similar (Fig. 3 and supporting information) and the parameters for the hydrogen bonds are nearly identical (Table 3). All the protons from the $[(NH_4 \cdot H_2O)]^+$ pair are contributing to six different hydrogen bonds (two sets of six bonds for the two independent molecules in **2**), which can be further divided into 4 two centered and 2 three centered hydrogen bonds. Both sulfur atoms from the PS_2^- unit and the oxygen atom from the water molecule act as acceptor atoms in these bonds. For clarity, only the acceptor atom type and not the symmetry code will be noted in the following lines. The two centered hydrogen bonds involve protons H(3) (acceptor O) and H(4) (acceptor S) from the ammonium cation, H(5) (acceptor S) and H(6) (acceptor S) from the water molecule (for **1** and molecule 1 of **2**), the protons H(9) (acceptor O) and H(10) (acceptor S) from the second ammonium cation and H(11) (acceptor S) and H(12) (acceptor S) from the second molecule of water in **2**. These hydrogen bonds have the values of the D–H⋯A angle of 165–176° and the H⋯A separation 1.92–1.97 Å (acceptor O) or 2.41–2.49 Å (acceptor S), respectively, and can be thus considered as strong [4a,18]. The three centered hydrogen bonds are asymmetric and involve the remaining N–H protons H(1) (acceptors S, S), H(2) (acceptors O – main component, S – minor component) for **1** and molecule 1 of **2**,
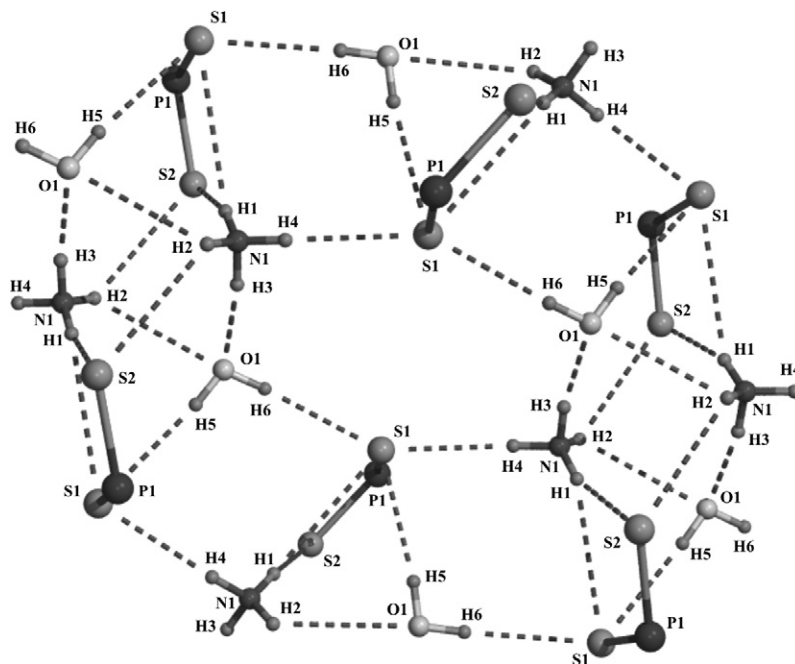

Fig. 4. Detail of the hydrogen bonding in the crystal of **1**. View along the *a* cell axis. All organic residues and the symmetry codes have been omitted for clarity.

and H(7) (acceptors S, S), H(8) (acceptors O – main component, S – minor component) in molecule 2 of **2**. The binding of the protons to two instead of one acceptor atom is obvious from the similar H···A distances in all six bonds present in **1** and **2** (2.49–2.68 Å for the major and 2.94–3.03 Å for the minor component) and is also reflected in less obtuse values for the D–H···A angles – 111–155°. Furthermore, as mentioned above, values of 3 Å are commonly accepted for the minor component of a three centered hydrogen bonds in proteins [18], thus, we can consider **1** and **2** as complexes containing asymmetric three centered hydrogen bond having sulfur atoms as the acceptors. The sulfur atom S(1) is involved in four hydrogen bonds (3 two centered and 1 three centered), whereas the atom S(2) acts as an acceptor in 2 three centered hydrogen bonds. For a full list of the parameters and details of these hydrogen bonds, see Table 3. A detail of the hydrogen bonding pattern with a numbering scheme for compound **1** is shown in Fig. 4. The fact, that it is not possible to dehydrate **1** and **2** back to **1a** and **2a** in vacuum at ambient temperature, demonstrates the stability of this 2D network formed solely by hydrogen bonds. The conversion of **1** and **2** back to **1a** and **2a** can be however achieved by heating **1** and **2** in vacuum for 5 h at 70 °C.

4. Concluding remarks

In summary, we have prepared two chemically and crystallographically different systems containing nearly identical 2D network formed by wide hydrogen bonding between water molecules, ammonium ions and $[(RO)(Fc)P(S)_2]^-$ units. These systems are valuable sources of information regarding the sulfur acceptor properties in hydrogen bonds and can serve as unique models for biological systems.

Acknowledgements

Appendix A. Supplementary material

CCDC 619853 and 619854 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi: doi:10.1016/j.jorganchem.2007.08.014.

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(b) The cations in the following structures are not located on any symmetry element: EXENUQ, KELXII, and ZODKAE.

[15] By definition, the two-centered hydrogen bond contains only one acceptor atom attached to the hydrogen atom, whereas there are two acceptor atoms attached to one hydrogen atom in a three-centered hydrogen bond. These three-centered hydrogen bonds can be either symmetric – both acceptor atom in comparable distance from the hydrogen atom – or asymmetric. In the asymmetric three-centered hydrogen bonds, there are major and minor components. The Major component futures shorter H$\cdots$acceptor distance than the minor component.

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