

Crystal structures and supramolecular assembly of 1:2 piperazine with *o*- and *p*-nitrophenol

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1:2 Cocrystals of piperazine (PPN) with *o*- and *p*-nitrophenol (oNPH and pNPH) were obtained from aqueous solution. The co-crystal structure of PPN, 2pNPH, and 2H₂O is triclinic space group $P\bar{1}$: $a = 6.401(1)$ Å, $b = 6.7515(1)$ Å, $c = 11.219(1)$ Å, $\alpha = 100.37(1)^\circ$, $\beta = 97.10(1)^\circ$, $\gamma = 99.99(1)^\circ$, $V = 465.5(1)$ Å³, $Z = 2$. Refinement led to a final conventional R value of 0.0365 for 2081 reflections. PPN, 2oNPH, and 2H₂O cocrystallize in the monoclinic space group $P2_1$: $a = 7.753(1)$ Å, $b = 10.888(2)$ Å, $c = 11.378(2)$ Å, $\beta = 92.89(1)^\circ$, $V = 953.1(3)$ Å³, $Z = 2$. Refinement led to a final conventional R value of 0.0347 for 1978 reflections. It was found in both cocrystals that the hydroxyl H-atom of pNPH and oNPH was transferred to a N-atom of PPN, forming new ionic complexes $PPNH_2^{2+} \cdot 2(oNP^-)$ and $PPNH_2^{2+} \cdot 2(pNP^-)$, respectively.

KEY WORDS: Piperazine; nitrophenol; crystal; hydrogen bond; supramolecular.

Introduction

Much effort has been devoted in the past decade to the study, design, and understanding of supramolecular networks.¹⁻³ The considerable interest in the field has been based on the fact that in crystal engineering, arrangement can be used to tailor materials of biological or technological importance.⁴ The formation of ordered solid-state networks relies on appropriate building blocks which have well-defined polyfunctional groups that can recognize complementary func-

tional groups on other like molecules (homomeric assembly) or on different molecules (heteromeric assembly). A crucial property of a building block is its ability to participate in noncovalent intermolecular interactions that are strong and highly directional relative to competing ones.

Piperazine (PPN), a difunctional amine, can be used as a potential building block to assemble supermolecular networks. Loehlin *et al.* have investigated its cocrystal structure with monofunctional phenol and found a chain of piperazine rings linked by phenol molecules in interesting eight-member hydrogen-bonded rings.⁵ However, the formation of extended networks requires "polyvalent" building blocks that are molecules having more than one binding functionality. The molecules containing multiple hydrogen binding functionalities can provide these capabilities.⁶ In view of this consideration, we attempt to use difunctional *p*-nitrophenol (pNPH)

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and *o*-nitrophenol (oNPH), instead of the mentioned single functional phenol, with PPN to assemble new extended supramolecular networks. In this paper, we report the synthesis, crystal structures, and analyses of their supramolecular features in these crystals.

Experimental

Materials

Piperazine (PPN), *p*-nitrophenol (PNPH), and *o*-nitrophenol (ONPH) were commercially available and used without further purification as starting materials. Crystal growth and data collection was carried out at room temperature.

Synthesis of $PPNH_2^{2+} \cdot 2(oNP^-) \cdot 2H_2O$

Large orange-red hexagonal plate crystals were grown by slow evaporation by following mixing of stoichiometric amounts of separate aqueous solution of PPN and oNPH.

Synthesis of $PPNH_2^{2+} \cdot 2(pNP^-) \cdot 2H_2O$

Yellow blocklike crystals were grown by the method mentioned above.

Structure determination and solution

The structures were determined using a Siemens P4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation at $\lambda = 0.71073$ Å. A semiempirical absorption correction via Ψ scans was applied. Each structure was solved by direct methods and refined anisotropically on F^2 by full-matrix least-squares techniques using the SHELXTL97 program.⁷ Experimental details of the X-ray structural determination for $PPNH_2^{2+} \cdot 2(pNP^-) \cdot 2H_2O$ and $PPNH_2^{2+} \cdot 2(oNP^-) \cdot 2H_2O$ are given in Table 1. Atomic coordinates, selected bond lengths, and angles are listed in Tables 2–5, respectively.

Results and discussion

$PPNH_2^{2+} \cdot 2(pNP^-) \cdot 2H_2O$

In this crystal hydroxyl H-atom of pNPH is transferred to a N-atom of PPN, leading to the formation of a new ionic complex that consists of a divalent $PPNH_2^{2+}$ cation and two univalent pNP^- anions. The ionic complex has an approximate asymmetric linear orientation as shown in Fig. 1, and the distance between the phenol oxygen and PPN nitrogen atom is 2.672(2) Å, exhibiting the strongest intermolecular interaction in this crystal. The distance is obviously shorter than that between the corresponding O and N in the cocrystal of piperazine and phenol (2.683(3) and 2.685(8) Å), in which no hydrogen-atom transfer was observed.⁵ The discrepancy can be attributed apparently to the enhancement in acidity of the phenol hydroxyl group with the introduction of the nitro group, which is a strong electron-withdrawing moiety.

The ionic complex acts as a new building block to form supramolecular networks. As shown in Fig. 2, adjacent ionic complexes are linked with each other via pNP^- and by the π - π stack interaction of phenol rings with a distance of 3.647 Å and two asymmetric ($PPNH_2^{2+}$) C—H...O(nitro) hydrogen bonds (3.114(2) Å), forming an infinite one-dimensional (1D) ionic complex chain. The remaining nitro O-atom in the 1D supramolecular chain binds $PPNH_2^{2+}$ in the adjacent chain via a C—H...O hydrogen bond (3.214(2) Å), resulting in the formation of an extended 2D supramolecular layer. Thus the nitro group plays an important role in forming the supramolecular layer. It not only causes H-atom transfer between PPN and phenol, but also participates in constructing both the supramolecular chain and layer through C—H...O bonds.

Packing analysis shows that water molecules do not take part in the chain formation of the ionic complexes but enhance the stability of the 2D supramolecular layer via a bridge of hydrogen bonds, $(pNP^-)O^- \cdots H-O(H_2O) \cdots H-N^+(PPNH_2^{2+})$, in which H_2O is a

Table 1. Crystallographic Data for $\text{PPNH}_2^{2+} \cdot 2(\text{pNP}^-) \cdot 2\text{H}_2\text{O}$ and $\text{PPNH}_2^{2+} \cdot 2(\text{oNP}^-) \cdot 2\text{H}_2\text{O}$

	$0.5[\text{PPNH}_2^{2+} \cdot 2(\text{pNP}^-) \cdot 2\text{H}_2\text{O}]$	$\text{PPNH}_2^{2+} \cdot 2(\text{oNP}^-) \cdot 2\text{H}_2\text{O}$
Formula weight	200.20	400.39
CCDC deposit no.	CCDC-1003/6132	CCDC-1003/6133
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1$
Cell dimension, mm	$0.44 \times 0.40 \times 0.20$	$0.46 \times 0.44 \times 0.44$
Lattice parameters		
a , Å	6.401(1)	7.753(1)
b , Å	6.715(1)	10.888(2)
c , Å	11.219(1)	11.378(2)
α , deg	100.37(1)	90
β , deg	92.89(1)	97.10(1)
γ , deg	99.99(1)	90
V , Å ³	465.5(1)	953.1(3)
Temp., K	295(2)	295(2)
Z	1	2
D (calculated), Mg/m ³	1.428	1.395
Radiation, Å	0.71073 (Mo $K\alpha$)	0.71073 (Mo $K\alpha$)
Scan mode	ω scan	ω scan
Data collection limits, deg	$1.80 \leq \theta \leq 26.00$	$1.80 \leq \theta \leq 26.00$
Limiting indices	$0 \leq h \leq 7, -8 \leq k \leq 8,$ $-14 \leq l \leq 14$	$0 \leq h \leq 9, 0 \leq k \leq 13,$ $-14 \leq l \leq 13$
Total unique reflections	2354	2204
Independent reflections	2081	1978
R_{int}	0.0117	0.013
Number of variables	136	276
Goodness of fit on F^2	0.953	0.963
R	0.0365	0.0347
wR	0.0930	0.0791
Largest diff. peak and hole	0.162 and -0.156	0.173 and -0.143
ρ , e ⁻ /Å ³	0.033	0.036

H-atom donor as well as a H-atom acceptor. At the same time, a remaining H-atom of H_2O hydrogen-bonds O^- of pNP^- in the adjacent supramolecular layer to assemble a 3D hydrogen-bonded network as shown in Fig. 2. The length of the hydrogen bonds is 2.82(12) Å, longer than that of the mentioned $(\text{pNP}^-)\text{O}^- \cdots \text{H}-\text{O}(\text{H}_2\text{O})$ that stabilizes 2D crystal framework (2.74 (12) Å).

It is unexpected that the nitro O-atom group binds only the H—C of PPNH_2^{2+} , not water, although H_2O is better donor than H—C. This may be due to the synergic effect of the C—H \cdots O(nitro) bond relative to π – π stack interaction of phenol ring and to geometrical preference. This observation further indicates that the hydrogen-bond selectivity and the donor–acceptor complementarity and preferences cannot be ex-

plained merely by acidity and basicity of the functional group.^{8,9}

$\text{PPNH}_2^{2+} \cdot 2(\text{oNP}^-) \cdot 2\text{H}_2\text{O}$

Similar to the cocrystal of PPN and pNPH, it was also found in the cocrystal of PPN and oNPH that the hydroxyl H-atom of oNPH was transferred to the N atoms of PPN, forming another new ionic complex, $\text{PPNH}_2^{2+} \cdot 2(\text{oNP}^-)$ (Fig. 3). However, the ionic complex has some structural characteristics different from that of $\text{PPNH}_2^{2+} \cdot 2(\text{pNP}^-)$. The former is additionally stabilized by two (nitro) $\text{O}^- \cdots \text{H}-\text{N}^+(\text{PPNH}_2^{2+})$ hydrogen bonds with a length of 2.682(3) Å, in addition to interionic interaction, appearing as two seven-membered ring motifs. The hydrogen

Table 2. Atomic Coordinates (10^{-4}) and Equivalent Isotropic Displacement Parameters (10^3 \AA^2) for $\text{PPNH}_2^{2+} \cdot 2(\text{pNP}^-) \cdot 2\text{H}_2\text{O}$

Atom	x	y	z	$U(\text{eq})^a$
O(1)	4034(2)	6015(2)	6922(2)	38(1)
O(2)	2702(3)	3752(2)	6307(2)	54(1)
O(3)	1428(4)	2868(3)	7634(2)	81(1)
O(4)	732(2)	3361(2)	3057(2)	41(1)
O(5)	2028(3)	5608(2)	3732(2)	51(1)
O(6)	2924(3)	6635(2)	2318(2)	67(1)
N(1)	2466(3)	3632(2)	7349(2)	44(1)
N(2)	1997(3)	5827(2)	2673(2)	43(1)
N(3)	4417(3)	9832(2)	4730(2)	37(1)
N(4)	955(3)	9520(2)	5309(2)	38(1)
C(1)	4124(3)	5533(3)	7979(2)	35(1)
C(2)	4924(4)	6174(3)	8966(2)	50(1)
C(3)	5013(5)	5726(3)	10103(3)	56(1)
C(4)	4302(4)	4608(3)	10333(2)	53(1)
C(5)	3462(4)	3956(3)	9414(2)	46(1)
C(6)	3388(3)	4390(3)	8254(2)	37(1)
C(7)	284(3)	3946(3)	2060(2)	36(1)
C(8)	-821(4)	3395(3)	1131(3)	52(1)
C(9)	-1285(5)	3974(4)	70(3)	62(1)
C(10)	-678(5)	5139(4)	-149(3)	65(1)
C(11)	381(4)	5716(3)	720(2)	54(1)
C(12)	849(4)	5149(3)	1807(2)	39(1)
C(13)	3594(4)	10786(3)	5405(2)	41(1)
C(14)	2271(4)	10227(3)	6102(2)	42(1)
C(15)	1792(4)	8554(3)	4640(3)	42(1)
C(16)	3100(3)	9134(3)	3943(2)	42(1)
O(7W)	437(3)	6121(2)	6390(2)	55(1)
O(8W)	4309(3)	3238(2)	3468(2)	50(1)

^a $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

bonds cause a obvious rotation of *o*-nitro group with respect to the aromatic ring, and the dihedral angle between phenol and *o*-nitro group planes is 159.1° , much greater than that (3.3°) in $\text{PPNH}_2^{2+} \cdot 2(\text{pNP}^-)$ and there is a greater averaged dihedral angle between PPNH_2^{2+} and oNP^- (117.8°) while $2(\text{pNP}^-)$ binds PPNH_2^{2+} in an approximate linear motif via ionic interaction only. Comparing with the phenol, the nitro group increases the acidity of the hydroxyl group of oNP^- analogous to that of pNP^- , but the $\text{O}^- \cdots \text{N}^+$ distance between oNP^- and PPNH_2^{2+} ($2.682(3) \text{ \AA}$) is the same as that between the corresponding O and N atoms in the cocrystal of PPN with phenol⁴ and longer than that between the corresponding O and N atoms in $\text{PPNH}_2^{2+} \cdot 2(\text{pNP}^-)$. The longer

$\text{O}^- \cdots \text{N}^+$ distance in $\text{PPNH}_2^{2+} \cdot 2(\text{oNP}^-)$ may be attributed to the steric hindrance of the nitro group located in the ortho position of hydroxyl group.

In the formation of PPN and oNP^- cocrystal, the new ionic complex $\text{PPNH}_2^{2+} \cdot 2(\text{oNP}^-)$ may be considered as a new building block. As shown in Fig. 3, the adjacent building blocks link via two related- H_2O hydrogen bonds, $(\text{ONP}^-)\text{O}^- \cdots \text{H}-\text{O}(\text{H}_2\text{O}) \cdots \text{H}-\text{N}^+(\text{PPNH}_2^{2+})$, forming a 1D supramolecular chain. In the two hydrogen bonds, H_2O is not only a H-atom donor of one ionic complex but also a H-atom acceptor of another, acting as a bridge connecting building blocks. The nitrophenol moieties of these 1D supramolecular chains are linking each other to assemble a

Table 3. Atomic Coordinates (10^{-4}) and Equivalent Isotropic Displacement Parameters (10^3 \AA^2) for $\text{PPNH}_2^{2+} \cdot 2(\text{ONP}^-) \cdot 2\text{H}_2\text{O}$

Atom	x	y	z	$U(\text{eq})^a$
O(1)	4034(2)	6015(2)	6922(2)	38(1)
O(2)	2702(3)	3752(2)	6307(2)	54(1)
O(3)	1428(4)	2868(3)	7634(2)	81(1)
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O(5)	2028(3)	5608(2)	3732(2)	51(1)
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C(1)	4124(3)	5533(3)	7979(2)	35(1)
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C(5)	3462(4)	3956(3)	9414(2)	46(1)
C(6)	3388(3)	4390(3)	8254(2)	37(1)
C(7)	284(3)	3946(3)	2060(2)	36(1)
C(8)	-821(4)	3395(3)	1131(3)	52(1)
C(9)	-1285(5)	3974(4)	70(3)	62(1)
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C(11)	381(4)	5716(3)	720(2)	54(1)
C(12)	849(4)	5149(3)	1807(2)	39(1)
C(13)	3594(4)	10786(3)	5405(2)	41(1)
C(14)	2271(4)	10227(3)	6102(2)	42(1)
C(15)	1792(4)	8554(3)	4640(3)	42(1)
C(16)	3100(3)	9134(3)	3943(2)	42(1)
O(7W)	437(3)	6121(2)	6390(2)	55(1)
O(8W)	4309(3)	3238(2)	3468(2)	50(1)

^a $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $\text{PPNH}_2^{2+} \cdot 2(\text{pNP}^-) \cdot 2\text{H}_2\text{O}$

Bond length		
O(1)—C(1)	1.3097(15)	
O(2)—N(1)	1.2294(17)	
O(3)—N(1)	1.2284(17)	
O(4W)—H(4A)	0.823(19)	
O(4W)—H(4B)	0.86(2)	
N(1)—C(4)	1.4373(17)	
N(2)—C(8)#1	1.4808(17)	
N(2)—C(7)	1.4865(16)	
C(1)—C(6)	1.408(2)	
C(1)—C(2)	1.410(2)	
C(2)—C(3)	1.3696(18)	
C(3)—C(4)	1.389(2)	
C(4)—C(5)	1.386(2)	
C(5)—C(6)	1.3662(19)	
C(7)—C(8)	1.5111(19)	
C(8)—N(2)#1	1.4808(17)	
Bond angle		
O(3)—N(1)—O(2)	121.77(13)	
O(3)—N(1)—C(4)	119.22(14)	
O(2)—N(1)—C(4)	119.00(14)	
C(8)#1—N(2)—C(7)	111.01(10)	
O(1)—C(1)—C(6)	121.50(13)	
O(1)—C(1)—C(2)	121.43(13)	
C(6)—C(1)—C(2)	117.07(12)	
C(3)—C(2)—C(1)	121.46(13)	
C(2)—C(3)—C(4)	119.38(13)	
C(5)—C(4)—C(3)	120.92(12)	
C(5)—C(4)—N(1)	119.89(13)	
C(3)—C(4)—N(1)	119.18(13)	
C(6)—C(5)—C(4)	119.22(13)	
C(5)—C(6)—C(1)	121.90(14)	
N(2)—C(7)—C(8)	111.08(12)	
N(2)#1—C(8)—C(7)	110.18(11)	

^aSymmetry transformations used to generate equivalent atoms: #1 $-x, -y, -z$.

2D supramolecular layer by a π - π stack interaction between the linked phenol rings (Fig. 4). It can be seen from Fig. 4 that except for one H_2O hydrogen atom and one nitro group oxygen atom, all other donors and acceptors are used for the formation of the 2D supramolecular layer, but the O^- of pNP^- has still one lone electron pair as a potential H-atom acceptor. These 2D supramolecular layers are connected into 3D supramolecular assembly via hydrogen bond between the lone electron pair and H_2O . Moreover it is also observed that H_2O as H-atom donor associates only with the phenol hydroxyl, not with nitro group, analogous to the situation in $\text{PPNH}_2^{2+} \cdot 2(\text{pNP}^-) \cdot 2\text{H}_2\text{O}$ crystal.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for $\text{PPNH}_2^{2+} \cdot 2(\text{pNP}^-) \cdot 2\text{H}_2\text{O}$

Bond length		
O(1)—C(1)	1.306(3)	
O(2)—N(1)	1.228(3)	
O(3)—N(1)	1.228(3)	
O(4)—C(7)	1.309(3)	
O(5)—N(2)	1.226(3)	
O(6)—N(2)	1.235(3)	
N(1)—C(6)	1.439(4)	
N(2)—C(12)	1.446(4)	
N(3)—C(16)	1.482(3)	
N(3)—C(13)	1.483(3)	
N(4)—C(14)	1.490(4)	
N(4)—C(15)	1.493(4)	
C(1)—C(2)	1.401(4)	
C(1)—C(6)	1.420(4)	
C(2)—C(3)	1.376(4)	
C(3)—C(4)	1.375(5)	
C(4)—C(5)	1.361(4)	
C(5)—C(6)	1.396(4)	
C(7)—C(8)	1.410(4)	
C(7)—C(12)	1.422(4)	
C(8)—C(9)	1.369(4)	
C(9)—C(10)	1.387(5)	
C(10)—C(11)	1.359(4)	
C(11)—C(12)	1.390(4)	
C(13)—C(14)	1.501(4)	
Bond angle		
O(3)—N(1)—O(2)	120.5(3)	
O(3)—N(1)—C(6)	18.9(2)	
O(2)—N(1)—C(6)	120.6(2)	
O(5)—N(2)—O(6)	121.2(3)	
O(5)—N(2)—C(12)	120.4(2)	
O(6)—N(2)—C(12)	118.4(2)	
C(16)—N(3)—C(13)	111.3(2)	
C(14)—N(4)—C(15)	111.4(2)	
O(1)—C(1)—C(2)	120.4(3)	
O(1)—C(1)—C(6)	125.3(3)	
C(2)—C(1)—C(6)	114.2(2)	
C(3)—C(2)—C(1)	122.9(3)	
C(4)—C(3)—C(2)	121.2(3)	
C(5)—C(4)—C(3)	118.7(3)	
C(4)—C(5)—C(6)	120.7(3)	
C(5)—C(6)—C(1)	122.3(3)	
C(5)—C(6)—N(1)	116.2(3)	
C(1)—C(6)—N(1)	121.5(2)	
O(4)—C(7)—C(8)	121.0(3)	
O(4)—C(7)—C(12)	124.6(3)	
C(8)—C(7)—C(12)	114.4(3)	
C(9)—C(8)—C(7)	122.3(3)	
C(8)—C(9)—C(10)	121.4(3)	
C(11)—C(10)—C(9)	118.7(3)	
C(10)—C(11)—C(12)	120.7(3)	
C(11)—C(12)—C(7)	122.4(3)	
C(11)—C(12)—N(2)	116.7(3)	
C(7)—C(12)—N(2)	120.8(3)	
N(3)—C(13)—C(14)	110.8(2)	
N(4)—C(14)—C(13)	110.6(2)	
N(4)—C(15)—C(16)	109.8(3)	
N(3)—C(16)—C(15)	110.9(2)	

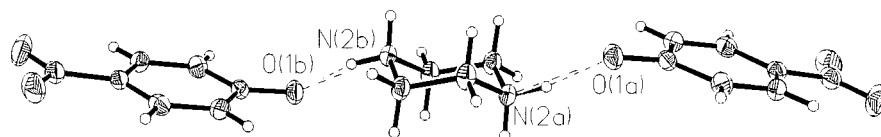


Fig. 1. Structure of ionic complex $\text{PPNH}_2^{2+} \cdot 2(\text{pNP}^-)$, with ellipsoids drawn at 50% probability. Water molecules are omitted for clarity.

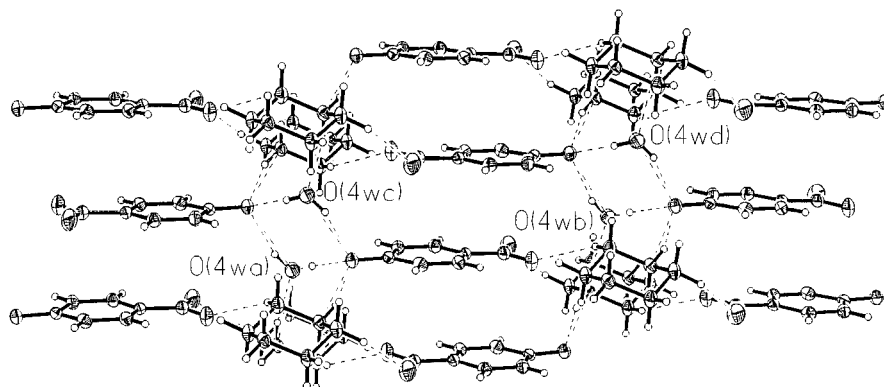


Fig. 2. View of hydrogen-bonded network of $\text{PPNH}_2^{2+} \cdot 2(\text{pNP}^-) \cdot 2\text{H}_2\text{O}$ along direction [100].

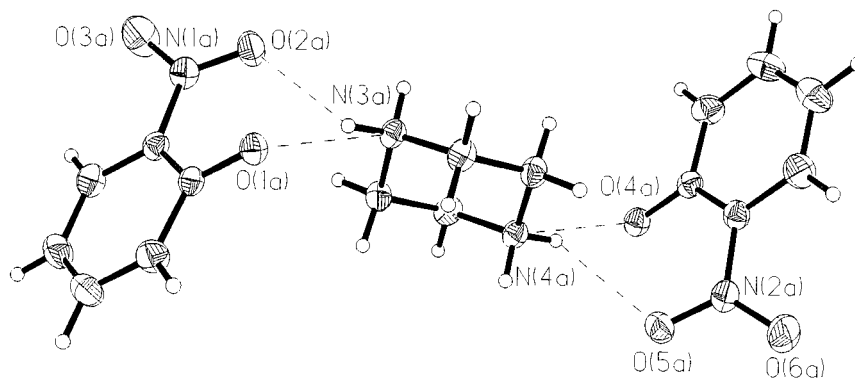


Fig. 3. Structure of ionic complex $\text{PPNH}_2^{2+} \cdot 2(\text{oNP}^-)$ with ellipsoids drawn at 45% probability. Water molecules are omitted for clarity.

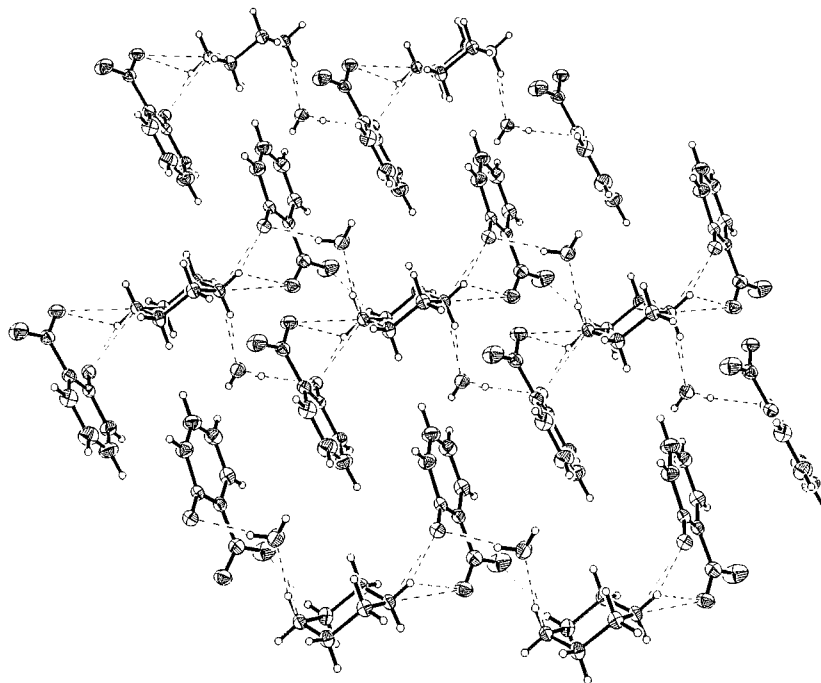


Fig. 4. Supramolecular layer of $\text{PPNH}_2^{2+} \cdot 2(\text{oNP}^-) \cdot \text{H}_2\text{O}$ parallel to plane (101).

Conclusion

Cocrystal structures of PPN with oNP or pNP are considerably different from that of PPN and phenol. In the present two cocrystals the hydroxyl H-atom of oNP and pNP is transferred to the N atoms of PPN, leading to the formation of two new ionic complexes or building blocks, $\text{PPNH}_2^{2+} \cdot 2(\text{oNP}^-)$ and $\text{PPNH}_2^{2+} \cdot 2(\text{pNP}^-)$. The analysis of these crystal structures shows that although ionic forces are in general long-range interaction and their nondirectional character limits their usefulness for molecular arrangement and control,⁷ the ionic force in ionic complex generated from H-atom transfer has some directional character and the ionic complex remembers some or most of hydrogen-bond information stored in their parent compounds possibly. Possibly it is the properties of these ionic complexes that make them extremely useful for recognition and supramolecular design.

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