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Rare examples of base pairing *via* a protonated pyridine N atom in two salts of N^2,N^6-bis(1,3-dimethylimidazolin-2-ylidene)pyridine-2,6-diamine

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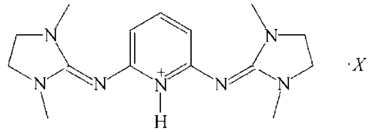
The title compounds, namely 2,6-bis[(1,3-dimethylimidazolin-2-ylidene)amino]pyridinium perchlorate, $C_{15}H_{24}N_7^+ \cdot ClO_4^-$, (I), and bis{2,6-bis[(1,3-dimethylimidazolin-2-ylidene)amino]-pyridinium} μ-oxido-bis[trichloridoiron(III)], $(C_{15}H_{24}N_7)_2[Fe_2Cl_6O]$, (II), are structurally unusual examples of the organization of molecular units *via* base pairing. The cations in salts (I) and (II) are derived from the bisguanidine N^2,N^6-bis(1,3-dimethylimidazolin-2-ylidene)pyridine-2,6-diamine, which associates in centrosymmetric pairs *via* two N—H$\cdots$N hydrogen-bond interactions. N—H$\cdots$N bridges are formed between the protonated pyridine N atom and one of the nonprotonated guanidine N atoms, with N$\cdots$H distances of 2.01 (1)–2.10 (1) Å. Compound (I) contains two crystallographically independent cations and anions per asymmetric unit. One of the perchlorate anions is disordered, while the $[Fe_2Cl_6O]^{2-}$ anion lies on an inversion centre.

Comment

The development of discrete dimeric, trimeric and other higher-order ensembles is a significant field of research, with possible applications in materials chemistry and nanotechnology. Furthermore, base pairs must be considered as playing a salient role in such critical areas as genetic coding, biological information storage and protein synthesis (Sessler *et al.*, 2007). During the synthesis of biomimetic complexes using iron and manganese salts, as well as ligands containing two guanidine (gua) N-donor functions and one pyridine N atom [N^2,N^6-bis(1,3-dimethylimidazolidin-2-ylidene)pyridine-2,6-diamine; Herres-Pawlis *et al.*, 2005; Neuba *et al.*, 2008], we synthesized the title compounds, (I) and (II), which display an interesting base-pair arrangement in the crystal structure.

The C_{gua}–N formal single bonds in (I), with a mean bond length of 1.340 (4) Å, have essentially the same length as the C5=N3 and C11=N5 double bonds [average 1.327 (4) Å]. In (II), the corresponding C_{gua}—N and C=N bonds have average lengths of 1.343 (3) and 1.323 (3) Å, respectively. Thus, the guanidyl double bonds in (I) and (II) are clearly delocalized over the three C—N bonds.



(I) $X = ClO_4^-$
(II) $X = 0.5Fe_2OCl_6^{2-}$

Similar delocalization of the guanidyl double bonds is observed in the protonated form of bis(tetramethylguanidino)biphenyl (Pruszynski *et al.*, 1992), but with a protonated N_{gua} atom instead. 2-Cyanoguanidine, with C—N bonds in the range 1.3327–1.3441 Å (Hirshfeld & Hope, 1980), also shows delocalization, but this is due to the cyano groups attached to the imine N atom. Localized C=N bond lengths in nonprotonated bisguanidine ligands range from 1.276 Å in *N*,*N*′-bis(dipiperidin-1-ylmethylene)propane-1,3-diamine (Herres *et al.*, 2004) to 1.302 Å in 2′,2′-(2,2′-dithiodiphenylene)bis-

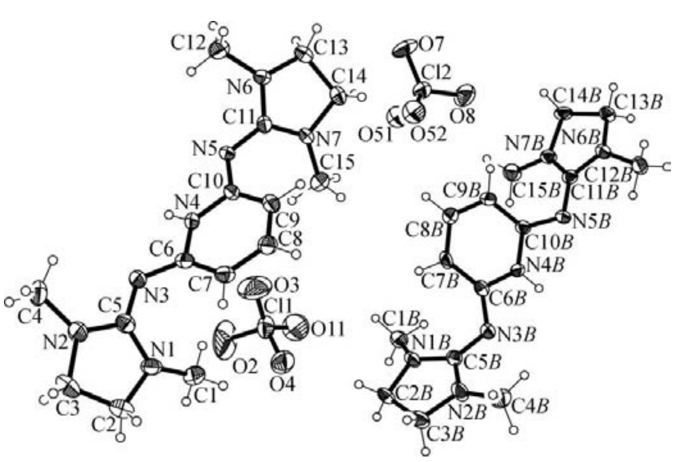


Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level.

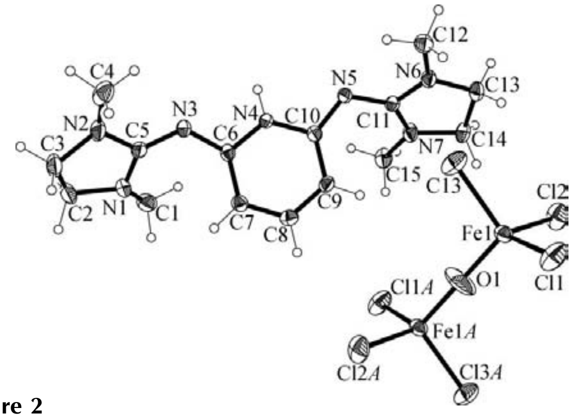


Figure 2
The molecular structure of (II). Displacement ellipsoids are drawn at the 50% probability level.

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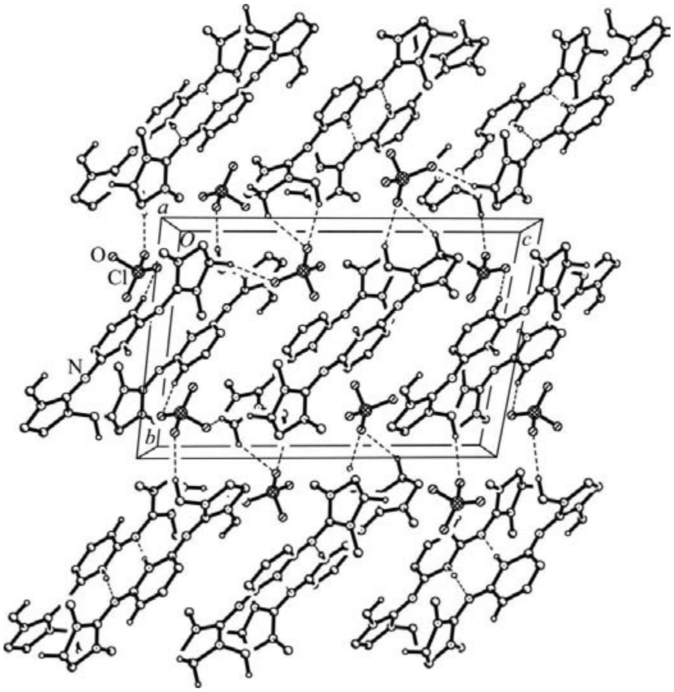

Figure 3
The crystal packing of (I), viewed along [100], with hydrogen bonds indicated as dashed lines. H atoms not involved in hydrogen bonds have been omitted. Only one orientation of each disordered perchlorate anion is shown.

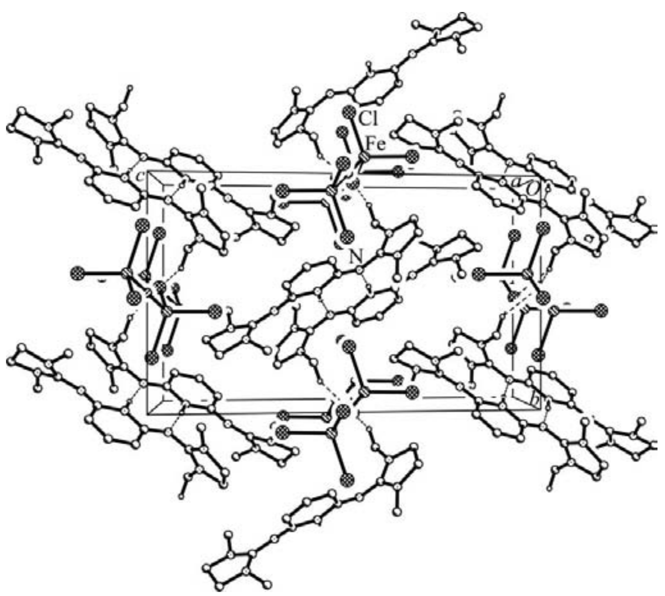

Figure 4
The crystal packing of (II), viewed along [100], with hydrogen bonds indicated as dashed lines. H atoms not involved in hydrogen bonds have been omitted.

(1,1,3,3-tetramethylguanidine) (Neuba *et al.*, 2007*b*). $C_{gua}-N$ single bond lengths vary from 1.362 Å in *N*,*N*′-bis(1,3-dimethylimidazolindin-2-ylidene)-2,2′-dithiodianiline (Neuba *et al.*, 2007*a*) to 1.407 Å in *N*,*N*′-bis(dipiperidin-1-ylmethylene)propane-1,3-diamine (Herres *et al.*, 2004).

Furthermore, the $C_{gua}-N_{gua}$ bond lengths in (I) and (II) are similar to the $N_{gua}-C_{py}$ and $C_{py}-N_{py}$ distances (py is pyridine). The pyridine ring and both guanidine units lie in a plane, showing that the guanidine delocalization is extended over the pyridine ring. In consequence, the protonation occurs at the N_{py} atom and not the N_{gua} atom, which indicates that the basicity of the N_{py} atom is increased compared with that of the N_{gua} atom. Normally, the N_{gua} position is found to be more basic. In this special case, the protonation leads to a pyridinium species, which is stabilized by mesomeric effects from both guanidyl units.

The exocyclic $N-C_{gua}-N$ angles show, for both structures, the same significant differences of 5.5–11.2° within each pair, but the angle sum at the C_{gua} atom in both (I) and (II) is 360°. Other geometric parameters of $C{=}N$, $C_{gua}-N$, $N_{gua}-C_{py}$ and $C_{py}-N_{py}$ for (I) and (II) are nearly identical (see Tables 1 and 3).

The crystal packing for both compounds (Figs. 1–4) is dominated by pairs of intermolecular hydrogen-bond interactions between protonated pyridine atom N4 and nonprotonated guanidine atom N5 of a centrosymmetrically related neighbouring molecule, stabilizing the structure with $N_{gua}\cdots H$ interactions of 2.007 (11) and 2.037 (11) Å in (I), and 2.096 (10) Å in (II). Additionally, these dimers form weak $C-H\cdots O$ and $C-H\cdots Cl$ bridges to the respective anions in (I) and (II). Thus, the packing pattern of (II) features infinite –dimer–anion–dimer– chains along [010]. For geometric details, see Tables 2 and 4.

Similarly generated dimers incorporating $N_{py}-H$ and $C{=}N$ functions are reported for 2-hydroxy(5-{[4-(2-pyridinylamino)sulfonyl]phenyl}azo)benzoic acid–*N*,*N*-dimethylformamide–water (1/0.5/*n*) (van der Sluis & Spek, 1990), 2-(nitroamino)pyridine (Angelova *et al.*, 1998) and ethyl 3-[4,5-dimethoxy-2-(4-methyl-2-pyridylsulphamoyl)phenyl]propionate (Eliopoulos *et al.*, 1983). The hydrogen-bond lengths in these structures range from 1.839 to 1.950 Å.

Similar dimers formed *via* $N-H\cdots N$ hydrogen bonds are reported for 2-(4-bromophenyl)-1,2-dihydropyrimido[1,2-*a*]benzimidazol-4(3*H*)-one and 4-(4-methylphenyl)-3,4-dihydropyrimido[1,2-*a*]benzimidazol-2(1*H*)-one (Low, Cobo, Insuasty *et al.*, 2002). Here, the hydrogen bonds are formed between an aliphatic $N-H$ group and a $C{=}N$ group, with $N\cdots H$ distances ranging from 1.98 to 2.30 Å. Similar geometries are observed in 2,2-dimethyl-1,2,3,4-tetrahydrobenzimidazo-[3,2-*a*]pyrimid-4-one, with a hydrogen-bond length of 2.18 Å (Bird *et al.*, 1991), and 2-phenyl-5-*p*-tolyl-1,5,6,10b-tetrahydropyrazolo[1,5-*c*]quinazoline, 5-(4-bromophenyl)-2-phenyl-1,5,6,10b-tetrahydropyrazolo[1,5-*c*]quinazoline and 2-(4-chlorophenyl)-5-phenyl-1,5,6,10b-tetrahydropyrazolo[1,5-*c*]quinazoline, with an average $N\cdots H$ distance of 2.23 Å (Low, Cobo, Nogueras *et al.*, 2002).

Experimental

The synthesis of *N*^{2},*N*^{6}-bis(1,3-dimethylimidazolidin-2-ylidene)pyridine-2,6-diamine is described in the literature (Herres-Pawlis *et al.*, 2005). For the preparation of (I), a solution of $Mn(ClO_4)_2\cdot6H_2O$ (362 mg, 1 mmol) in MeCN (7 ml) was treated at room temperature with *N*^{2},*N*^{6}-bis(1,3-dimethylimidazolidin-2-ylidene)pyridine-2,6-di amine (331 mg, 1.1 mmol). The clear solution was stirred for 1 h, and diffusion of Et_2O gave colourless crystals suitable for X-ray diffraction after 3 d. IR (KBr, ν, cm^{-1}): 3486 (*s*), 2949 (*w*), 2871 (*w*), 1617 (*m*), 1585 (*vs*, C═N), 1536 (*vs*, C═N), 1448 (*s*), 1417 (*m*), 1382 (*s*), 1294 (*m*), 1240 (*w*), 1166 (*m*), 960 (*m*), 838 (*s*), 557 (*m*). For the preparation of (II), a solution of $FeCl_2$ (127 mg, 1 mmol) in CH_2Cl_2 (10 ml) was treated at room temperature with *N*^{2},*N*^{6}-bis(1,3-dimethylimidazolidin-2-ylidene)pyridine-2,6-diamine (331 mg, 1.1 mmol) to yield a yellow solution. After 30 min under reflux, the solution was filtered and allowed to stand in air. After 2 d, red crystals suitable for X-ray diffraction were obtained. IR (KBr, ν, cm^{-1}): 3423 (*m*), 2935 (*w*), 2875 (*w*), 1629 (*m*), 1596 (*vs*, C═N), 1562 (*s*, C═N), 1520 (*vs*), 1479 (*s*), 1446 (*m*), 1390 (*s*), 1361 (*s*), 1295 (*m*), 1250 (*s*), 1165 (*s*), 1049 (*m*), 960 (*m*), 877 (*w*), 785 (*w*), 673 (*m*), 569 (*w*).

Compound (I)

Crystal data

$C_{15}H_{24}N_7^+\cdot ClO_4^-$
M_r = 401.86
Triclinic, $P\overline{1}$
a = 10.4399 (11) Å
b = 12.0367 (13) Å
c = 16.6200 (18) Å
α = 95.979 (2)°
β = 93.739 (2)°
γ = 115.549 (2)°
V = 1859.9 (3) Å^3
Z = 4
Mo *Kα* radiation
μ = 0.24 mm^{-1}
T = 120 (2) K
0.35 × 0.20 × 0.18 mm

Data collection

Bruker SMART APEX diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
$T_{\min}$ = 0.920, $T_{\max}$ = 0.960
18737 measured reflections
8994 independent reflections
3686 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.092

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.064
$wR(F^2)$ = 0.147
S = 0.83
8994 reflections
499 parameters
9 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$ = 0.72 e Å^{-3}
$\Delta\rho_{\min}$ = −0.45 e Å^{-3}

Compound (II)

Crystal data

$(C_{15}H_{24}N_7)_2[Fe_2Cl_6O]$
M_r = 945.22
Monoclinic, $P2_1/c$
a = 10.5673 (8) Å
b = 10.9286 (8) Å
c = 18.3329 (14) Å
β = 99.438 (2)°
V = 2088.5 (3) Å^3
Z = 2
Mo *Kα* radiation
μ = 1.12 mm^{-1}
T = 120 (2) K
0.43 × 0.25 × 0.20 mm

Data collection

Bruker SMART APEX diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
$T_{\min}$ = 0.644, $T_{\max}$ = 0.806
20962 measured reflections
5142 independent reflections
3929 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.066

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.113
S = 0.98
5142 reflections
249 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$ = 0.96 e Å^{-3}
$\Delta\rho_{\min}$ = −0.72 e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

N1—C5	1.342 (4)	N1*B*—C5*B*	1.350 (4)
N2—C5	1.352 (4)	N2*B*—C5*B*	1.334 (4)
N3—C5	1.318 (4)	N3*B*—C5*B*	1.319 (4)
N3—C6	1.355 (4)	N3*B*—C6*B*	1.348 (4)
N4—C10	1.352 (4)	N4*B*—C10*B*	1.352 (4)
N4—C6	1.354 (4)	N4*B*—C6*B*	1.366 (4)
N5—C11	1.337 (4)	N5*B*—C11*B*	1.341 (4)
N5—C10	1.350 (4)	N5*B*—C10*B*	1.357 (4)
N7—C11	1.331 (4)	N6*B*—C11*B*	1.344 (4)
N6—C11	1.338 (4)	N7*B*—C11*B*	1.340 (4)
N3—C5—N1	130.3 (3)	N3*B*—C5*B*—N2*B*	120.9 (3)
N3—C5—N2	120.5 (3)	N3*B*—C5*B*—N1*B*	129.1 (3)
N1—C5—N2	109.1 (3)	N2*B*—C5*B*—N1*B*	109.9 (3)
N7—C11—N5	127.7 (3)	N7*B*—C11*B*—N5*B*	127.9 (3)
N7—C11—N6	109.9 (3)	N7*B*—C11*B*—N6*B*	109.9 (3)
N5—C11—N6	122.3 (3)	N5*B*—C11*B*—N6*B*	122.2 (3)

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4···N5$^{\rm i}$	0.881 (10)	2.007 (11)	2.885 (4)	175 (3)
N4*B*—H4*B*···N5*B*$^{\rm ii}$	0.888 (10)	2.037 (11)	2.922 (4)	174 (3)
C1—H10*E*···O2$^{\rm iii}$	0.98	2.41	3.229 (5)	141
C2—H10*J*···O2$^{\rm iii}$	0.99	2.45	3.219 (5)	134
C1*B*—H20*F*···O7$^{\rm iv}$	0.98	2.44	3.301 (4)	146

Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $-x+2, -y+1, -z+2$; (iii) $-x+1, -y+2, -z+1$; (iv) $x+1, y+1, z$.

Table 3
Selected geometric parameters (Å, °) for (II).

N1—C5	1.345 (3)	N4—C6	1.370 (2)
N2—C5	1.362 (3)	N5—C11	1.337 (2)
N3—C5	1.308 (3)	N5—C10	1.348 (3)
N3—C6	1.351 (3)	N6—C11	1.321 (3)
N4—C10	1.360 (3)	N7—C11	1.343 (3)
N3—C5—N1	130.9 (2)	N6—C11—N5	121.62 (18)
N3—C5—N2	119.7 (2)	N6—C11—N7	110.44 (17)
N1—C5—N2	109.37 (19)	N5—C11—N7	127.80 (19)

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4···N5$^{\rm i}$	0.871 (10)	2.096 (10)	2.964 (2)	174 (3)
C1—H1*A*···Cl1$^{\rm ii}$	0.98	2.96	3.816 (3)	146
C1—H1*C*···Cl2$^{\rm iii}$	0.98	2.94	3.716 (3)	137
C12—H12*C*···Cl3$^{\rm iv}$	0.98	2.83	3.469 (2)	123

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x, y+1, z$; (iii) $x, -y+\frac{1}{2}, z+\frac{1}{2}$; (iv) $-x+1, -y, -z+1$.

Pyridine N-bound H atoms were refined with N—H distance restraints of 0.88 (1) Å. All other H atoms were refined at idealized positions, riding on their parent C atoms, with $U_{\rm iso}$(H) parameters of $1.2U_{\rm eq}$(C) or $1.5U_{\rm eq}(CH_3)$. All methyl H atoms were allowed to rotate but not to tip. The disordered perchlorate anion of (I) was refined with an isotropic split model for O-atom positions O11/O12, O51/O52 and O61/O62, each with a site-occupation factor of 0.5.

For both compounds, data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXL97*; software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: EM3010). Services for accessing these data are described at the back of the journal.

References

Angelova, O., Petrova, R. & Atanasov, V. (1998). *Acta Cryst.* C**54**, 441–442.

Bird, C. W., Nyburg, S. C. & Parkins, A. W. (1991). *Acta Cryst.* C**47**, 1943–1945.

Bruker (2002). *SMART* (Version 5.62) and *SAINT* (Version 6.02). Bruker AXS Inc., Madison, Wisconsin, USA.

Eliopoulos, E., Sheldrick, B. & Hamodrakas, S. (1983). *Acta Cryst.* C**39**, 743–745.

Herres, S., Flörke, U. & Henkel, G. (2004). *Acta Cryst.* C**60**, o358–o360.

Herres-Pawlis, S., Neuba, A., Seewald, O., Seshadri, T., Egold, H., Flörke, U. & Henkel, G. (2005). *Eur. J. Org. Chem.* pp. 4879–4890.

Hirshfeld, F. L. & Hope, H. (1980). *Acta Cryst.* B**36**, 406–415.

Low, J. N., Cobo, J., Insuasty, B., Nogueras, M., Salcedo, A. & Sánchez, A. (2002). *Acta Cryst.* C**58**, o125–o128.

Low, J. N., Cobo, J., Nogueras, M., Sánchez, A., Torres, H. & Insuasty, B. (2002). *Acta Cryst.* C**58**, o305–o310.

Neuba, A., Flörke, U. & Henkel, G. (2007*a*). *Acta Cryst.* E**63**, o3476–o3477.

Neuba, A., Flörke, U. & Henkel, G. (2007*b*). *Acta Cryst.* E**63**, o4661.

Neuba, A., Herres-Pawlis, S., Flörke, U. & Henkel, G. (2008). *Z. Anorg. Allg. Chem.* **634**, 771–777.

Pruszynski, P., Leffek, K. T., Borecka, B. & Cameron, T. S. (1992). *Acta Cryst.* C**48**, 1638–1641.

Sessler, J. L., Lawrence, C. M. & Jayawickramarajah, J. (2007). *Chem. Soc. Rev.* **36**, 314–325.

Sheldrick, G. M. (2004). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Sluis, P. van der & Spek, A. L. (1990). *Acta Cryst.* C**46**, 883–886.