

***N,N'*-Bis(dipiperidin-1-ylmethylene)-propane-1,3-diamine and *N,N'*-bis(1,3-dimethylperhydropyrimidin-2-ylidene)propane-1,3-diamine**

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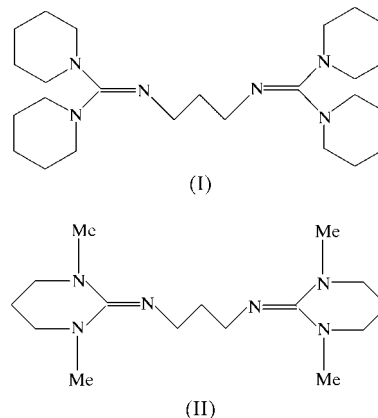
The molecular structures of the title compounds, $C_{25}H_{46}N_6$ and $C_{15}H_{30}N_6$, respectively, show the two guanidyl moieties each connected by propyl bridges. The different substitution pattern of the guanidyl groups has no influence on the distinct localization of their $C=N$ double bonds. Both compounds exhibit approximate twofold symmetry and the crystal packing shows no prominent hydrogen-bonding interactions.

Comment

In the search for bifunctional N-donor ligands able to stabilize unusually high metal oxidation states, we have extended our studies to guanidyl-type systems. The first derivative, the ligand bis(tetramethylguanidino)propylene (btmgp), and its complexes with Cu, Fe and Ni, have recently been investigated (Harmjanz, 1997; Waden, 1999; Pohl *et al.*, 2000; Schneider, 2000; Herres, 2002). We have now developed the title compounds, (I) [a piperidine derivative, bis(dipiperidylguanidino)propylene] and (II) [a propylene derivative, 1,3-bis(dimethylpropyleneguanidino)propane], as novel ligands for use in biomimetic coordination chemistry. In Cu–O₂ chemistry in particular, the modification of the guanidyl moieties within the ligands is expected to control the formation of different Cu–O₂ species (Herres *et al.*, 2004).

The molecule of (I) lies roughly on a non-crystallographic twofold axis running through C13, with a *trans* arrangement of the guanidyl groups relative to the C12–C13–C14 centre. The resulting torsion angles are N1–C12–C13–C14 = 70.3 (1)° and N4–C14–C13–C12 = 68.8 (1)°. The C–N single bonds range from 1.392 (1) to 1.404 (1) Å, while the C=N double bonds, C1=N1 and C14=N4, have similar values, with a mean of 1.276 (1) Å. The mean of the N2–C1–N3 and N5–C15–N6 angles is 113.91 (10)°, and the mean of the C1–N1–C12 and C15–N4–C14 angles is 119.88 (9)°. Thus, the guanidyl double bonds in (I) are clearly localized. The same is valid for the related compound (II). Here, the

corresponding C–N single-bond lengths range from 1.375 (3) to 1.407 (3) Å, and the mean of the C6=N3 and C10=N4 double bonds is 1.284 (2) Å. The mean of the N1–C6–N2 and N5–C10–N6 angles is 114.8 (2)°, and the mean of the C6–N3–C7 and C9–N4–C10 angles is 119.5 (2)°.



Similar double-bond localization is observed in bis(tetramethylguanidino)naphthalene (Raab *et al.*, 2002), with equally unprotonated imine N and NR₂ amino groups having a mean C=N bond length of 1.282 (3) Å and a mean C–N bond length of 1.384 (1) Å. In bis(tetramethylguanidino)biphenyl (Pruszyński *et al.*, 1992), with a protonated imine N atom, strong delocalization is observed among the three C–N bonds, which are in the range 1.31 (1)–1.34 (1) Å. 2-Cyano-guanidine, with C–N bonds in the range 1.3327 (3)–1.3441 (3) Å (Hirshfeld & Hope, 1980), and, to a lesser extent, tetrabenzylcyanoguanidine, with C=N = 1.315 Å and C–N = 1.370 Å (no s.u. values given; Shiba *et al.*, 1993), also show delocalization, but this is due to the cyano groups attached to the imine N atom. Substitution of the NH₂ groups in cyanoguanidine with NBz₂ (Bz is benzyl) leads to the observed increase in localization.

For compound (I), the shortest non-bonding intramolecular C–H...N distance is C14–H14B...N5, with H...N = 2.45 Å,

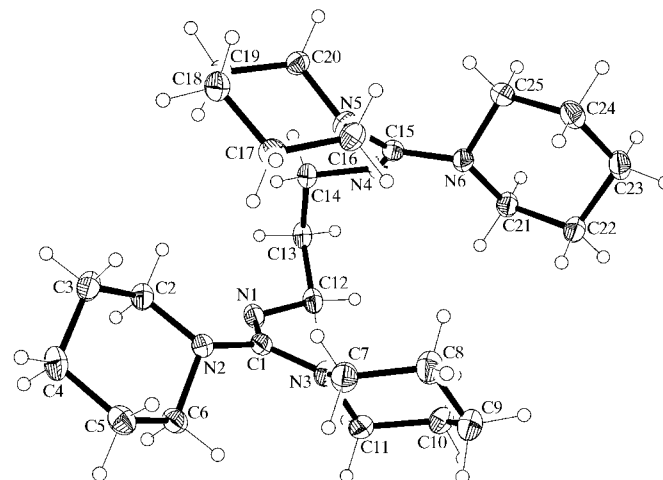


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

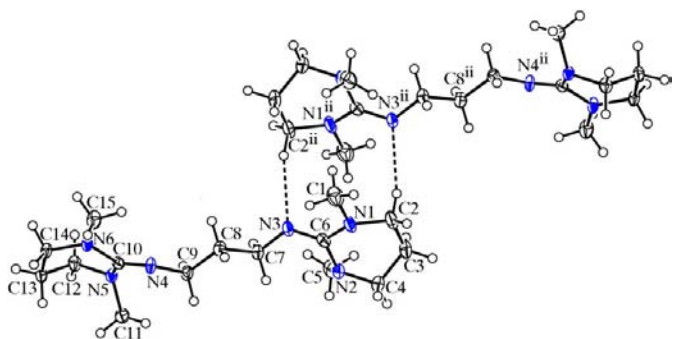


Figure 2
The molecular structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The $C2 \cdots N3^{ii}$ interaction is depicted [symmetry code: (ii) $-x, 2 - y, -z$].

while the shortest intermolecular distance results from a $C4-H4A \cdots N4^i$ interaction, with $H \cdots N = 2.86 \text{ \AA}$ [symmetry code: (i) $x + \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$]. For compound (II), the corresponding distances are $C2-H2B \cdots N3^{ii} = 2.62 \text{ \AA}$ (Fig. 2) and $C12-H12B \cdots N2^{iii} = 2.68 \text{ \AA}$ [symmetry codes: (ii) $-x, 2 - y, -z$; (iii) $x + 1, y - 1, z$]. The former interaction generates a hydrogen-bonded dimer with graph set $R_2^2(10)$ (Fig. 2).

Experimental

Compound (I) was prepared as follows: a solution of *N,N,N',N'*-dipiperidylchloroformamidinium chloride (7.53 g, 30 mmol) in dry MeCN was added dropwise under vigorous stirring to an ice-cooled solution of 1,3-diaminopropane (1.11 g, 15 mmol) and triethylamine (4.18 ml, 3.03 g, 30 mmol) in dry MeCN. After 3 h under reflux, a solution of NaOH (1.2 g, 30 mmol) in water was added. The solvents and NEt_3 were then evaporated under vacuum. In order to deprotonate the bis-hydrochloride, 50 wt% KOH (aqueous, 15 ml) was added and the free base was extracted into the MeCN phase (3 \times 20 ml). The organic phase was dried with Na_2SO_4 over charcoal. After filtration over Celite, the solvent was evaporated under reduced pressure. The pure product, (I), was obtained as a white powder (yield 66%, 4.26 g). Colourless crystals of (I) suitable for X-ray diffraction were obtained by crystallization from a cold saturated MeCN solution. Spectroscopic analysis, 1H NMR (500 MHz, $CDCl_3$): δ 1.48–1.61 (*m*, 24H, Pip- CH_2), 1.80 (*q*, 2H, CH_2), 3.02 (*t*, 16H, Pip- CH_2), 3.18 (*t*, 4H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$): δ 24.8 (Pip), 25.9 (Pip), 34.5 (C13), 46.7 (C12, C14), 49.1 (Pip), 160.0 (C quart.); IR (KBr, ν , cm^{-1} , important bands): 2927 (*vs*), 1626 (*vs*, $C=N$), 1608 (*s*, $C=N$), 1398 (*s*), 1367 (*s*), 1246 (*s*), 1209 (*s*); EI-MS: m/z (%) 430 (42) [M^+], 346 (10) [$M^+ - Pip$], 237 (13), 222 (81), 196 (12), 154 (41), 126 (43), 85 (51) [HPip], 84 (100) [Pip], 69 (22). Compound (II) was prepared as follows: a solution of *N,N'*-dimethylpropylenechloroformamidinium chloride (7.33 g, 40 mmol) in dry MeCN was added dropwise under vigorous stirring to an ice-cooled solution of 1,3-diaminopropane (1.48 g, 20 mmol) and triethylamine (5.57 ml, 4.04 g, 40 mmol) in dry MeCN. After 3 hours under reflux, a solution of NaOH (1.6 g, 40 mmol) in water was added. Further treatment was carried out as for (I). The pure product, (II), was obtained as a colourless oil which crystallized after two months, giving needles suitable for X-ray diffraction (yield 92%, 5.4 g, 18.4 mmol). Spectroscopic analysis, 1H NMR (500 MHz, $CDCl_3$): δ 1.50 (*m*, 2H, CH_2), 1.68 (*m*, 4H, CH_2), 2.70 (*s*, 12H, CH_3), 2.95 (*m*, 8H, CH_2), 3.02 (*t*, 4H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.9 (CH_2), 32.3 (C8), 39.3

(CH_3), 45.8 (C7, C9), 48.4 (CH_2), 157.5 (C quart.); IR (KBr, ν , cm^{-1} , important bands): 2921 (*s*), 2858 (*s*), 1621 (*vs*, $C=N$), 1576 (*s*, $C=N$), 1541 (*s*); CI-MS: m/z 294 (25) [M^+]. The formamidinium salts were prepared according to the literature procedures of Kantlehner *et al.* (1984).

Compound (I)

Crystal data

$C_{25}H_{46}N_6$
 $M_r = 430.68$
Monoclinic, $P2_1/n$
 $a = 10.0619$ (7) \AA
 $b = 19.8127$ (13) \AA
 $c = 12.7511$ (8) \AA
 $\beta = 99.594$ (2) $^\circ$
 $V = 2506.4$ (3) \AA^3
 $Z = 4$

$D_x = 1.141 \text{ Mg m}^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 3799 reflections
 $\theta = 2.3\text{--}27.5^\circ$
 $\mu = 0.07 \text{ mm}^{-1}$
 $T = 120$ (2) K
Prism, colourless
 $0.40 \times 0.35 \times 0.20 \text{ mm}$

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2002)
 $T_{min} = 0.951$, $T_{max} = 0.989$
19 511 measured reflections
6205 independent reflections

4055 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.044$
 $\theta_{max} = 28.3^\circ$
 $h = -13 \rightarrow 13$
 $k = -22 \rightarrow 26$
 $l = -12 \rightarrow 17$
3843 standard reflections
intensity decay: $<1\%$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.090$
 $S = 0.86$
6205 reflections
280 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0397P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.22 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.15 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$) for (I).

N1—C1	1.2753 (14)	N4—C14	1.4629 (13)
N1—C12	1.4616 (13)	N5—C15	1.3924 (13)
N2—C1	1.4039 (14)	N6—C15	1.4002 (13)
N3—C1	1.3999 (14)	C12—C13	1.5144 (16)
N4—C15	1.2776 (13)	C13—C14	1.5171 (15)
C1—N1—C12	120.24 (9)	C12—C13—C14	111.42 (9)
C15—N4—C14	119.52 (9)	N4—C14—C13	109.23 (9)
N1—C1—N3	125.94 (10)	N4—C15—N5	125.82 (10)
N1—C1—N2	120.11 (10)	N4—C15—N6	120.12 (10)
N3—C1—N2	113.86 (10)	N5—C15—N6	113.95 (9)
N1—C12—C13	109.44 (9)	C12—N1—C1—N2	165.14 (9)
C12—N1—C1—N2	165.14 (9)	C14—N4—C15—N6	163.03 (9)
C6—N2—C1—N1	117.55 (12)	C25—N6—C15—N4	122.44 (11)

Compound (II)

Crystal data

$C_{15}H_{30}N_6$
 $M_r = 294.45$
Triclinic, $P\bar{1}$
 $a = 6.9057$ (7) \AA
 $b = 7.6661$ (7) \AA
 $c = 16.3568$ (16) \AA
 $\alpha = 89.307$ (3) $^\circ$
 $\beta = 82.355$ (2) $^\circ$
 $\gamma = 73.152$ (2) $^\circ$
 $V = 821.07$ (14) \AA^3

$Z = 2$
 $D_x = 1.191 \text{ Mg m}^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 718 reflections
 $\theta = 2.5\text{--}21.1^\circ$
 $\mu = 0.08 \text{ mm}^{-1}$
 $T = 120$ (2) K
Prism, colourless
 $0.20 \times 0.15 \times 0.10 \text{ mm}$

Table 2
Selected geometric parameters (Å, °) for (II).

N1—C6	1.375 (3)	N4—C9	1.464 (2)
N2—C6	1.407 (3)	N5—C10	1.393 (3)
N3—C6	1.279 (2)	N6—C10	1.385 (2)
N3—C7	1.453 (3)	C7—C8	1.518 (3)
N4—C10	1.289 (2)	C8—C9	1.510 (3)
C6—N3—C7	119.93 (19)	C9—C8—C7	112.94 (19)
C10—N4—C9	119.16 (19)	N4—C9—C8	110.21 (18)
N3—C6—N1	119.2 (2)	N4—C10—N6	118.5 (2)
N3—C6—N2	125.9 (2)	N4—C10—N5	126.45 (19)
N1—C6—N2	114.7 (2)	N6—C10—N5	114.86 (18)
N3—C7—C8	110.09 (19)		
C7—N3—C6—N2	12.8 (3)	C9—N4—C10—N5	16.4 (3)

Data collection

Bruker SMART CCD area-detector diffractometer	1931 reflections with $>2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.047$
Absorption correction: multi-scan (SADABS; Bruker, 2002)	$\theta_{\text{max}} = 28.3^\circ$
$T_{\text{min}} = 0.910$, $T_{\text{max}} = 0.989$	$h = -8 \rightarrow 9$
7147 measured reflections	$k = -9 \rightarrow 10$
4053 independent reflections	$l = -21 \rightarrow 21$
	726 standard reflections
	intensity decay: <1%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0224P)^2 + 0.0587P]$
$R[F^2 > 2\sigma(F^2)] = 0.054$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.113$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 0.84$	$\Delta\rho_{\text{max}} = 0.23 \text{ e } \text{Å}^{-3}$
4053 reflections	$\Delta\rho_{\text{min}} = -0.17 \text{ e } \text{Å}^{-3}$
194 parameters	
H-atom parameters constrained	

For both compounds, all H atoms were placed in calculated positions, with C—H distances of 0.99 Å in (I) and 0.98 and 0.99 Å in (II),

and refined as riding on their attached C atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1207). Additional figures are also available. Services for accessing these data are described at the back of the journal.

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