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Disorder in *n*-Alkyl Ammonium Dihydrogen Phosphate Crystals: C_{*n*}H_{2*n*+1}NH₃⁺.H₂PO₄⁻

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Abstract

Two homologues of a new family of the *n*-alkylammonium dihydrogen phosphate crystals, *n*-heptyl C₇H₁₅NH₃⁺.H₂PO₄⁻ (C7ADP) and *n*-octyl C₈H₁₇NH₃⁺.H₂PO₄⁻ (C8ADP), have been analysed by single-crystal X-ray diffraction. At room temperature, the crystals are ferroelastics with a dense lamellar domain structure when observed under a polarizing microscope. The crystal structures are characterized by the arrangement of the planar all-*trans* *n*-alkylammonium chains and disordered PO₄ tetrahedra. The organic chains are linked to the H₂PO₄ anions through a system of N—H...O hydrogen bonds. The phase transitions at *T_c* = 344 K in C7ADP and *T_c* = 362 K in C8ADP are related to the dynamics of the constituent structural groups.

Comment

The title compounds, reported recently by Kroupa & Fuith (1993, 1994), belong to the new wide group of ammonium dihydrogen phosphate (NH₄H₂PO₄) related materials in which the ammonium ions are substituted by alkyl chains of various lengths (C_{*n*}H_{2*n*+1}NH₃⁺; *n* = 1–9, 12). Studies of the optical indicatrix orientation and the thermal dependence of birefringence, together with the results of measurements of the dielectric constant and the thermal dilatation, have revealed interesting physical properties of these crystals connected with numerous phase transitions (Kroupa & Fuith, 1993).

The structures of the compounds with *n* = 7 (C7ADP) and *n* = 8 (C8ADP) are characterized by an arrangement of antiparallel planar organic chains along the *b* axis interdistributed with the inorganic units. The *n*-alkylammonium chains have all-*trans* zigzag conformations with no significant departures from regular geometry (Fig. 1, Tables 2 and 4),

whereas the phosphate groups are partly disordered between two equivalent orientations relative to the local mirror plane passing through the P and O(1) atoms (Fig. 2). The P—O distances vary from 1.474 (7) to 1.569 (8) Å in C7ADP and from 1.498 (6) to 1.578 (7) Å in C8ADP.

Although both structures have been analysed with the standard choice of the unit cell in *P*2₁/*c*, the two resulting models differ in the relative arrangement of the organic and inorganic units. A superposition of the two structures can be obtained assuming a non-standard unit cell with the monoclinic angle β' = (180° – β) for C8ADP. This difference can be related to the results of the optical measurements (Kroupa & Fuith, 1993); the angle φ denoting the orientation of the optical indicatrix in the two adjacent domains is 75° in C7ADP and 11.5° in C8ADP, *i.e.* they are almost complementary.

The crystal structures of C7ADP and C8ADP at room temperature provide a helpful reference in understanding the mechanism of the phase transi-

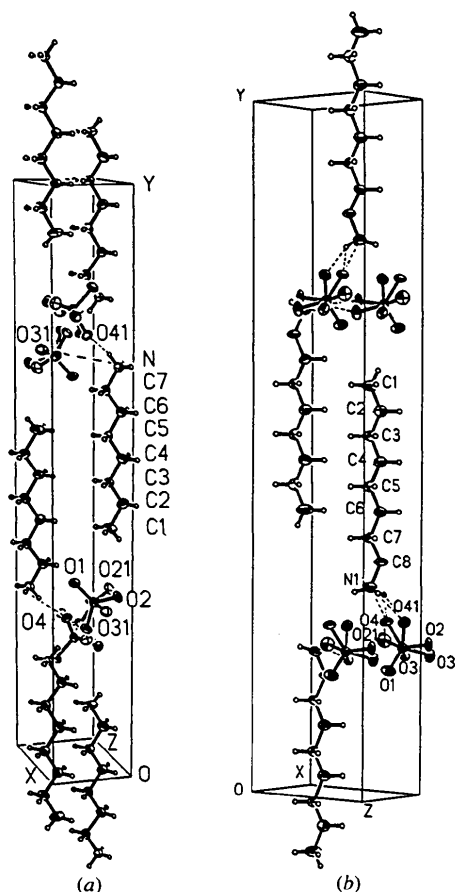


Fig. 1. The crystal structures of (a) C₇H₁₅NH₃⁺.H₂PO₄⁻ and (b) C₈H₁₇NH₃⁺.H₂PO₄⁻ with 50% probability displacement ellipsoids for non-H atoms. H atoms are drawn as circles of arbitrary size.

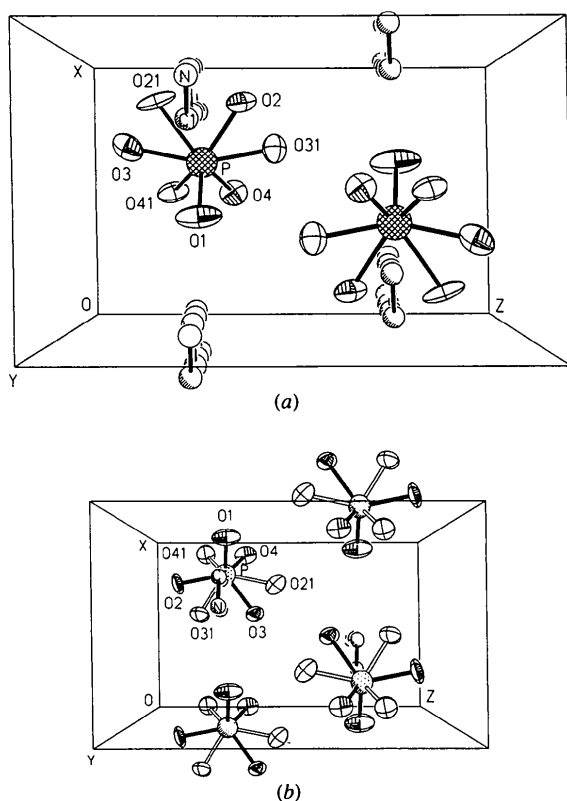


Fig. 2. Perspective drawings of (a) $C_7H_{15}NH_3^+ \cdot H_2PO_4^-$ and (b) $C_8H_{17}NH_3^+ \cdot H_2PO_4^-$ viewed down the b axis. The PO_4 groups are shown in their disordered shape (with and without octant reading). H atoms are omitted for clarity.

tions in this material. At room temperature, the fine domain structure can be interpreted in terms of the local disorder, static or dynamic, of the PO_4 tetrahedra. Either two neighbouring domains contain unit cells with the two opposing PO_4 configurations, or a flipping motion takes place between two equilibrium orientations with the probability $p = \pm 1$ in each domain. It is not possible to differentiate unequivocally between static and dynamic disorder although it seems that the relatively high value of the dielectric constant, measured in the direction perpendicular to the domain walls (Kroupa & Fuith, 1993), is more suggestive of dynamic disorder. The fact that split PO_4 groups are observed in both crystals (with different alkylammonium chain lengths) suggests that the disorder is not directly dependent on the number (even or odd) of C atoms in the chains. The reason may, however, lie in the thermal displacements of the light terminal NH_3 and CH_3 groups. This motion is strongly anisotropic and has the same character in both structures, *i.e.* the highest displacement amplitudes lie in the (ac) plane corresponding to the flipping direction of the O atoms (Fig. 2).

The range of $N \cdots O$ distances at room temperature is quite large [2.767 (8)–2.964 (12) Å in C7ADP, 2.765 (1)–2.984 (10) Å in C8ADP (Table 5)] but the average is not far from 2.75 Å, the distance considered to correspond to a medium–strong hydrogen bond of this type (*e.g.* Blessing, 1986). In both structures, there is a hydrogen-bond linkage between the PO_4 groups and the organic part as a result of the formation of the $P-O \cdots H-N$ bonds. Although the two acid H atoms could not be located, both the PO_4 and NH_3 groups are also in favourable positions to allow a $P-O-H \cdots N$ hydrogen bond. This hydrogen bond is expected to play an essential role in the low-temperature phase.

At temperatures above T_c (~ 344 and 362 K for C7ADP and C8ADP, respectively), an abrupt decrease of the diffraction intensities and disappearance of the domain structure, accompanied by a considerable increase in the dielectric permittivity, has been observed. The permittivity reaches a relative value above 100, compared to about 25 at room temperature. A decay of the diffraction intensities above T_c makes an X-ray single-crystal structure determination impossible. However, the effects mentioned above strongly suggest that thermally activated motion of n -alkylammonium chains together with the flipping motions of the PO_4 groups induce the formation of the fully disordered structure. Considering the ferroelastic room-temperature phase as a deformation of the prototypical high-symmetry phase, we can extrapolate the symmetry of the paraelastic phase to be orthorhombic.

Experimental

The title compounds were prepared from methanol solutions of stoichiometric quantities of the n -alkylamine (pure, Fluka) and H_3PO_4 using the thermal-gradient method. The crystals obtained were thin transparent plates, frequently twinned. Viewed down the b axis in a polarizing microscope they showed ferroelastic fine-lamellar domain structure with the domain walls perpendicular to the a axis.

C7ADP

Crystal data

$C_7H_{18}N^+ \cdot H_2PO_4^-$
 $M_r = 213.2$
 Monoclinic
 $P2_1/c$
 $a = 4.577$ (1) Å
 $b = 32.074$ (6) Å
 $c = 7.353$ (1) Å
 $\beta = 90.74$ (3)°
 $V = 1079.4$ (3) Å³
 $Z = 4$
 $D_x = 1.312$ Mg m⁻³

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 37 reflections
 $\theta = 7\text{--}13^\circ$
 $\mu = 0.234$ mm⁻¹
 $T = 296$ K
 Sphere
 0.18 mm (radius)
 Colourless, transparent

Data collection

Kuma KM-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction:
 spherical
 $T_{\min} = 0.76$, $T_{\max} = 0.82$
 5869 measured reflections
 2508 independent reflections
 1071 observed reflections
 $[F > 4\sigma(F)]$

Refinement

Refinement on F
 $R = 0.056$
 $wR = 0.060$
 $S = 1.45$
 2508 reflections
 164 parameters
 $w = 1/[\sigma^2(F_o) + 0.000295(F_o^2)]$
 $(\Delta/\sigma)_{\max} = 0.178$
 $\Delta\rho_{\max} = 0.34 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.37 \text{ e } \text{\AA}^{-3}$

C8ADP**Crystal data**

C₈H₂₀N⁺.H₂PO₄⁻
 $M_r = 227.2$
 Monoclinic
 $P2_1/c$
 $a = 4.589 (2) \text{ \AA}$
 $b = 34.701 (7) \text{ \AA}$
 $c = 7.365 (3) \text{ \AA}$
 $\beta = 90.61 (3)^\circ$
 $V = 1172.8 (7) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.287 (1) \text{ Mg m}^{-3}$

Data collection

Kuma KM-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction:
 spherical
 $T_{\min} = 0.78$, $T_{\max} = 0.82$
 7637 measured reflections
 4427 independent reflections
 1512 observed reflections
 $[F > 4\sigma(F)]$

Refinement

Refinement on F
 $R = 0.065$
 $wR = 0.065$
 $S = 1.66$
 4427 reflections
 175 parameters
 $w = 1/[\sigma^2(F_o) + 0.00015(F_o^2)]$
 $(\Delta/\sigma)_{\max} = 0.111$
 $\Delta\rho_{\max} = 0.35 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.38 \text{ e } \text{\AA}^{-3}$

$R_{\text{int}} = 0.036$
 $\theta_{\max} = 36.5^\circ$
 $h = -7 \rightarrow 7$
 $k = -48 \rightarrow 48$
 $l = -9 \rightarrow 0$
 2 standard reflections
 monitored every 50
 reflections
 intensity decay: 2.2%

Extinction correction:
 $F_c = F(1 + 0.002\kappa F^2 / \sin^2\theta)^{-1/4}$
 (Larson, 1970)
 Extinction coefficient:
 $\kappa = 0.018$
 Atomic scattering factors
 from *International Tables*
 for *X-ray Crystallography*
 (1974, Vol. IV)

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 37
 reflections
 $\theta = 7-14^\circ$
 $\mu = 0.219 \text{ mm}^{-1}$
 $T = 296 \text{ K}$
 Sphere
 0.16 mm (radius)
 Colourless, transparent

$R_{\text{int}} = 0.032$
 $\theta_{\max} = 37.5^\circ$
 $h = 0 \rightarrow 7$
 $k = -49 \rightarrow 49$
 $l = -11 \rightarrow 11$
 2 standard reflections
 monitored every 50
 reflections
 intensity decay: 2%

Extinction correction:
 $F_c = F(1 + 0.002\kappa F^2 / \sin^2\theta)^{-1/4}$
 (Larson, 1970)
 Extinction coefficient:
 $\kappa = 0.00027$
 Atomic scattering factors
 from *International Tables*
 for *X-ray Crystallography*
 (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for C7ADP
$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j.$$

	x	y	z	U_{eq}
C(1)	0.8306 (14)	-0.0785 (2)	0.2537 (13)	0.056 (2)
C(2)	1.0087 (12)	-0.0378 (2)	0.2475 (10)	0.040 (1)
C(3)	0.8225 (10)	0.0005 (2)	0.2507 (11)	0.037 (1)
C(4)	0.9960 (12)	0.0410 (2)	0.2501 (11)	0.039 (1)
C(5)	0.8075 (10)	0.0801 (2)	0.2515 (11)	0.040 (1)
C(6)	0.9788 (10)	0.1206 (2)	0.2498 (11)	0.040 (1)
C(7)	0.7808 (10)	0.1585 (2)	0.2460 (9)	0.032 (1)
N	0.9450 (8)	0.1974 (1)	0.2489 (9)	0.041 (1)
P	0.3768 (3)	0.2952 (1)	0.2443 (3)	0.028 (1)
O(1)	0.6108 (8)	0.3305 (1)	0.2521 (10)	0.051 (1)
O(2)	0.1160 (12)	0.3076 (2)	0.1378 (12)	0.034 (2)
O(3)	0.3106 (14)	0.2888 (2)	0.4420 (12)	0.040 (2)
O(4)	0.5090 (14)	0.2542 (2)	0.1641 (12)	0.032 (2)
O(21)	0.1109 (12)	0.3094 (3)	0.3617 (14)	0.045 (2)
O(31)	0.3171 (14)	0.2885 (2)	0.0486 (11)	0.036 (2)
O(41)	0.5062 (13)	0.2542 (2)	0.3253 (12)	0.032 (3)

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for C8ADP
$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j.$$

	x	y	z	U_{eq}
N	0.3959 (9)	0.7013 (1)	0.2492 (8)	0.039 (2)
C(1)	0.4061 (16)	0.4093 (2)	0.2521 (10)	0.057 (2)
C(2)	0.2320 (12)	0.4464 (2)	0.2507 (9)	0.043 (2)
C(3)	0.4131 (11)	0.4827 (1)	0.2490 (8)	0.037 (2)
C(4)	0.2329 (11)	0.5198 (1)	0.2505 (8)	0.036 (2)
C(5)	0.4117 (11)	0.5564 (2)	0.2511 (8)	0.037 (2)
C(6)	0.2338 (10)	0.5929 (1)	0.2490 (8)	0.036 (2)
C(7)	0.4112 (10)	0.6301 (1)	0.2490 (7)	0.031 (2)
C(8)	0.2231 (10)	0.6653 (1)	0.2492 (8)	0.031 (2)
P(1)	0.1706 (3)	0.2920 (1)	0.2562 (2)	0.024 (1)
O(1)	-0.0661 (8)	0.3243 (1)	0.2481 (6)	0.041 (1)
O(2)	0.2328 (14)	0.2855 (2)	0.4538 (8)	0.032 (2)
O(3)	0.4319 (13)	0.3053 (2)	0.1391 (9)	0.029 (2)
O(4)	0.0395 (14)	0.2540 (2)	0.1761 (10)	0.030 (2)
O(31)	0.4366 (13)	0.3035 (2)	0.3638 (9)	0.035 (2)
O(41)	0.0344 (14)	0.2541 (2)	0.3381 (10)	0.033 (2)
O(21)	0.2380 (15)	0.2836 (2)	0.0544 (10)	0.038 (3)

Table 3. Selected geometric parameters (\AA , $^\circ$) for C7ADP

C(1)—C(2)	1.541 (8)	P—O(1)	1.560 (4)
C(2)—C(3)	1.496 (7)	P—O(2)	1.474 (7)
C(3)—C(4)	1.523 (7)	P—O(3)	1.502 (9)
C(4)—C(5)	1.522 (7)	P—O(4)	1.565 (8)
C(5)—C(6)	1.516 (7)	P—O(21)	1.569 (8)
C(6)—C(7)	1.517 (7)	P—O(31)	1.477 (8)
C(7)—N	1.457 (6)	P—O(41)	1.557 (8)
C(1)—C(2)—C(3)	113.2 (5)	O(1)—P—O(4)	110.8 (3)
C(2)—C(3)—C(4)	113.8 (4)	O(2)—P—O(4)	110.0 (4)
C(3)—C(4)—C(5)	114.0 (4)	O(3)—P—O(4)	109.5 (4)
C(4)—C(5)—C(6)	114.3 (4)	O(1)—P—O(21)	107.8 (4)
C(5)—C(6)—C(7)	112.2 (4)	O(1)—P—O(31)	105.0 (4)
C(6)—C(7)—N	112.2 (4)	O(1)—P—O(41)	110.0 (3)
O(1)—P—O(2)	111.9 (4)	O(21)—P—O(31)	116.3 (4)
O(1)—P—O(3)	102.2 (4)	O(21)—P—O(41)	109.2 (5)
O(2)—P—O(3)	112.3 (4)	O(31)—P—O(41)	108.4 (4)

Table 4. Selected geometric parameters (\AA , $^\circ$) for C8ADP

N—C(8)	1.479 (6)	P(1)—O(1)	1.563 (4)
C(1)—C(2)	1.515 (8)	P(1)—O(2)	1.498 (6)
C(2)—C(3)	1.507 (7)	P(1)—O(3)	1.554 (6)
C(3)—C(4)	1.530 (7)	P(1)—O(4)	1.563 (7)
C(4)—C(5)	1.513 (7)	P(1)—O(31)	1.502 (7)
C(5)—C(6)	1.507 (7)	P(1)—O(41)	1.578 (7)
C(6)—C(7)	1.526 (7)	P(1)—O(21)	1.550 (7)
C(7)—C(8)	1.495 (6)		

C(1)—C(2)—C(3)	114.7 (5)	O(1)—P(1)—O(4)	109.1 (3)
C(2)—C(3)—C(4)	113.8 (4)	O(2)—P(1)—O(4)	108.0 (4)
C(3)—C(4)—C(5)	114.5 (4)	O(3)—P(1)—O(4)	109.7 (4)
C(4)—C(5)—C(6)	114.4 (4)	O(1)—P(1)—O(31)	112.9 (3)
C(5)—C(6)—C(7)	115.0 (4)	O(1)—P(1)—O(41)	109.6 (3)
C(6)—C(7)—C(8)	112.5 (4)	O(1)—P(1)—O(21)	104.2 (3)
N—C(8)—C(7)	112.4 (4)	O(31)—P(1)—O(21)	112.8 (4)
O(1)—P(1)—O(2)	105.7 (3)	O(31)—P(1)—O(41)	110.0 (4)
O(1)—P(1)—O(3)	107.8 (3)	O(41)—P(1)—O(21)	107.0 (4)
O(2)—P(1)—O(3)	116.4 (4)		

Table 5. Hydrogen bonds (Å, °)

N—H...O	H...O	N...O	N—H...O
C7ADP			
N—H(1)...O(2 ⁱ)	2.242 (9)	2.960 (11)	146.0 (4)
N—H(1)...O(31 ⁱ)	1.986 (7)	2.805 (9)	173.8 (3)
N—H(2)...O(4)	1.932 (7)	2.767 (8)	153.8 (4)
N—H(2)...O(41)	1.910 (7)	2.774 (8)	160.5 (4)
N—H(3)...O(21 ⁱⁱ)	2.083 (10)	2.964 (12)	154.7 (3)
N—H(3)...O(3 ⁱⁱ)	1.929 (8)	2.861 (10)	168.8 (4)
C8ADP			
N—H(1)...O(2 ⁱⁱⁱ)	1.944 (7)	2.796 (9)	158.1 (4)
N—H(1)...O(31 ⁱⁱⁱ)	2.079 (8)	2.949 (10)	163.5 (4)
N—H(2)...O(4 ^{iv})	1.926 (6)	2.768 (8)	160.4 (4)
N—H(2)...O(41 ^v)	1.925 (6)	2.765 (8)	159.4 (4)
N—H(3)...O(21 ^v)	2.117 (11)	2.859 (8)	172.3 (3)
N—H(3)...O(3 ^v)	2.342 (12)	2.984 (10)	147.8 (5)

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

The crystal quality, preliminary cell constants and diffraction symmetry were determined from Weissenberg photographs (systematic absences: $h0l, l = 2n + 1$; $0k0, k = 2n + 1$) and optical indicatrix observations under a polarizing microscope. The samples selected for the intensity-data collection were ground into spheres; because of their ferroelasticity this was performed using wet blotting paper.

The structures were solved by direct methods. *E* maps revealed the positions of the P atom, one well defined atom of the H₂PO₄ group [O(1)] and all the non-H atoms forming the *n*-alkylammonium chain. After a full-matrix least-squares refinement of these fragments, using isotropic displacement factors, the $\Delta\rho$ map showed six peaks of electron density $\sim 4 \text{ e } \text{Å}^{-3}$ within the P coordination sphere. The *z* coordinates for pairs of these peaks were mirror related. Assuming partial disorder of the PO₄ group, the peaks were assigned to the three missing O atoms and then refined with the position occupancy factor *K* = 0.5 (*R* factors were 0.078 and 0.086 for C7ADP and C8ADP, respectively). The final $\Delta\rho$ maps revealed most H atoms of the *n*-alkylammonium chains except for those belonging to the terminal methyl and ammonium groups, which were placed in calculated positions. In the last stages of the refinement, positional parameters of all H atoms were fixed and only their isotropic temperature coefficients were refined. The two acid protons could not be localized unambiguously and were not included in the calculations.

Data collection, cell refinement and data reduction: *KM-4* (Kuma, 1992). Structure solution, refinement and molecular graphics: *SHELXTL/PC* (Sheldrick, 1990). Preparation of material for publication: *SHELXTL/PC* and local programs.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB0326). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tris(3,5-dimethylpyrazol-1-yl)methylsilane

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Abstract

The structure consists of discrete molecules of tris-(3,5-dimethylpyrazol-1-yl)methylsilane, C₁₆H₂₄N₆Si, that exhibit distorted tetrahedral SiN(pyrazole)₃C geometry about the Si atom. The Si and methyl C atoms lie on threefold axes. The C—Si—N and N—Si—N bond angles are 111.3 (2) and 107.5 (2)°, respectively, while the Si—N bond length is 1.745 (5) Å. The present work provides the first reported structure containing an Si—N(pyrazole) linkage.

Comment

As part of a long-term project designed to aid understanding of the structural and spectroscopic properties of the active sites of selected metalloproteins, we have prepared and characterized numerous low molecular weight analogues (Potenza, Stibrany, Potenza & Schugar, 1992). A particular challenge has been to prepare pseudo-tetrahedral or pseudo-C_{3v} complexes with Cu^{II}, an ion whose ligand field