

The cyclopentadienyl rings were idealized and refined as rigid groups. Some of the methoxy groups, especially the O atoms, have high *U* values.

Data collection: profile-fitting program (Clegg, 1981). Cell refinement: profile-fitting program. Data reduction: XLS (Sheldrick, 1987). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1985) using direct methods. Program(s) used to refine structure: XLS (Sheldrick, 1987). Molecular graphics: SHELXTL-Plus (Sheldrick, 1990). Software used to prepare material for publication: SHELXTL-Plus.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: JZ1119). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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trans-Diazidobis[1,2-bis(diethylphosphino)ethane-*P,P'*]iron(II)

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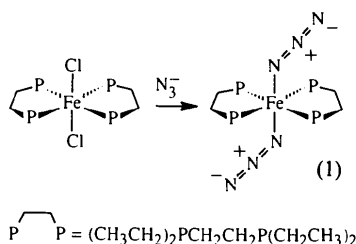
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Abstract

The title structure, [Fe(N₃)₂(C₁₀H₂₄P₂)₂], has been studied and was found to consist of neutral molecules with the Fe atom located at a centre of symmetry. The Fe—P bond lengths [2.258 (1) and 2.268 (1) Å] are indicative of low-spin Fe^{II}. The Fe—N_{azido} distance is 2.008 (4) Å.

Comment

As part of a project investigating the synthesis of iron tetraphosphines having acetylido, azido and nitrile ligands, a series of diazido complexes of the type [Fe(PP)₂(N₃)₂] [where PP is 1,2-bis(dimethylphosphino)ethane (dmpe), 1,2-bis(diethylphosphino)ethane (depe) or 1,2-bis(dipropylphosphino)ethane (dprpe)] were synthesized and their properties examined (Buys, Field, George, Hambley & Pike, 1995). These bis(diazido)–iron(II) complexes can easily be converted to the corresponding iron–bis(acetylide) complexes by reaction with the corresponding acetylene. The title compound, [Fe(depe)₂(N₃)₂], (1), was synthesized by substitution of the chloride in [FeCl₂(depe)₂] with azide in alcohol solution.



The crystal structure of (1) (Fig. 1) shows the three N atoms of each azide group to be approximately linear, with an Fe—N—N angle of 139.1 (4)°. This is significantly larger than the corresponding angle found in related structures, for example, 132.3 (3)° for Fe—N—N in [Fe(dmpe)₂(N₃)₂] (Buys, Field, George, Hambley & Pike, 1995), 121.8 (4)° for Fe—N—N in [Fe(tppe)(N₃)₂] (where tppe is tetraphenylporphyrin) (Zhang, Hallows, Ryan, Jones, Carpenter & Sweigart, 1994), 116.7 (7)° for Ru—N—N in [Ru(en)₂(N₂)(N₃)⁺] (Davis & Ibers, 1970), 132.9 (3)° for Ru—N—N in [Ru(N₃)₂(depe)₂] (Buys, Field, George, Hambley & Purches, 1995), 125.4 (5)° for Cu—N—N in [Cu{Et₂NCH₂CH₂N(H)CH₂CH₂NEt₂}₂(Br)(N₃)₂] (Ziolo, Allen, Titus, Gray & Dorio, 1972) and 121.4 (6)–129.9 (5)° for Mo—N—N in [Mo(N₃)₄(NO)(H₂NO)] (Weighardt, Backes-Dahmann, Swiridoff & Weiss, 1983). The N—N bond lengths are 1.170 (5) and 1.155 (6) Å for (Fe—)N₁—N₂ and (N—)N₂—N₃, respectively, which compare well with values of 1.179 (5) and 1.162 (5) Å for the corresponding bond lengths in [Fe(dmpe)₂(N₃)₂] (Buys, Field, George, Hambley & Pike, 1995), and values of 1.180 (5) and 1.170 (5) Å in [Ru(depe)₂(N₃)₂] (Buys, Field, George, Hambley & Purches, 1995). The N—N bond lengths in HN₃ are 1.240 (3) and 1.134 (3) Å (Amkle & Dailey, 1950), and 1.150 (16) Å in N₃[−] (Frevél, 1936). The azide groups in (1) are tilted in opposite directions in the crystal.

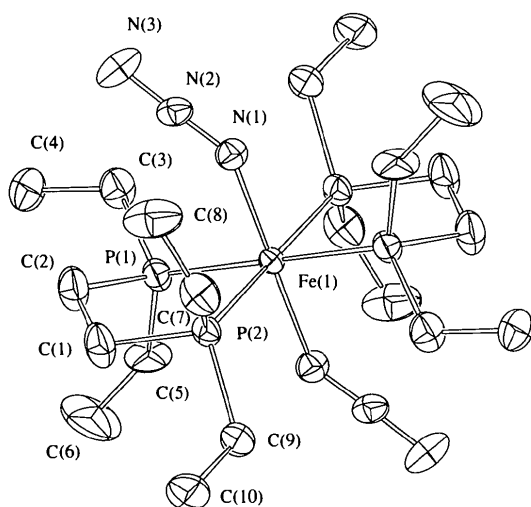


Fig. 1. ORTEP (Johnson, 1965) plot of (1) with ellipsoids at the 30% probability level. Only one of the disordered C(5)—C(6) components is shown.

Experimental

Details of the synthesis of (1) have been published elsewhere (Buys, Field, George, Hambley & Pike, 1995). The crystals of (1) used for the crystallographic analysis were obtained by slow evaporation of a toluene solution.

Crystal data

[Fe(N₃)₂(C₁₀H₂₄P₂)₂]

M_r = 552.38

Monoclinic

*P*2₁/*n*

a = 9.897 (2) Å

b = 13.746 (2) Å

c = 10.436 (2) Å

β = 99.81 (2)°

V = 1399.1 (4) Å³

Z = 2

D_x = 1.311 Mg m⁻³

Mo Kα radiation

λ = 0.7109 Å

Cell parameters from 25 reflections

θ = 10–12°

μ = 0.787 mm⁻¹

T = 294 K

Prism

0.110 × 0.090 × 0.025 mm

Blue–green

Data collection

Enraf–Nonius CAD-4 diffractometer

ω/2θ scans

Absorption correction:

analytical (De Meulenaer & Tompa, 1965)

T_{min} = 0.988, *T_{max}* = 0.996

2740 measured reflections

2675 independent reflections

1906 observed reflections

[*I* > 2.5σ(*I*)]

R_{int} = 0.04

θ_{max} = 25°

h = -11 → 11

k = 0 → 16

l = 0 → 12

3 standard reflections

frequency: 120 min

intensity decay: 13%

Refinement

Refinement on *F*²

R = 0.050

wR = 0.058

S = 2.26

w = 1/σ²(*F*)

(Δ/σ)_{max} = 0.05

Δρ_{max} = 0.5 e Å⁻³

Δρ_{min} = -0.4 e Å⁻³

1906 reflections
160 parameters
H-atom parameters not refined

Atomic scattering factors from TEXSAN (Molecular Structure Corporation, 1993)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B_{eq}</i>
Fe(1)	0	0	1/2	2.69 (3)
P(1)	-0.09531 (13)	0.10629 (9)	0.62340 (12)	3.62 (5)
P(2)	0.19760 (12)	0.03440 (9)	0.63727 (12)	3.45 (5)
N(1)	0.0372 (4)	0.1084 (3)	0.3820 (4)	4.1 (2)
N(2)	0.0224 (4)	0.1927 (3)	0.3720 (4)	4.1 (2)
N(3)	0.0118 (6)	0.2758 (4)	0.3583 (6)	7.0 (3)
C(1)	0.1700 (6)	0.1334 (4)	0.7470 (6)	5.7 (3)
C(2)	0.0404 (6)	0.1889 (4)	0.6995 (6)	5.7 (3)
C(3)	-0.2268 (6)	0.1927 (4)	0.5460 (6)	5.1 (3)
C(4)	-0.2584 (7)	0.2798 (4)	0.6236 (6)	6.4 (3)
C(5)†	-0.259 (3)	0.036 (2)	0.7628 (4)	8.1 (20)
C(5')†	-0.175 (3)	0.0614 (13)	0.7524 (15)	7.4 (15)
C(6)†	-0.118 (2)	0.0364 (16)	0.838 (4)	12.1 (20)
C(6')†	-0.169 (3)	0.0823 (18)	0.8828 (18)	12.0 (20)
C(7)	0.3529 (6)	0.0710 (5)	0.5782 (6)	5.9 (3)
C(8)	0.3518 (7)	0.1656 (6)	0.5116 (7)	8.5 (4)
C(9)	0.2656 (6)	-0.0605 (4)	0.7560 (6)	5.9 (3)
C(10)	0.3861 (7)	-0.0346 (5)	0.8589 (6)	6.9 (3)

† Occupancy of 0.5.

Table 2. Selected geometric parameters (Å, °)

Fe(1)—P(1)	2.258 (1)	Fe(1)—P(2)	2.268 (1)
N(1)—N(2)	1.170 (5)	N(2)—N(3)	1.155 (6)
Fe(1)—N(1)	2.008 (4)		
P(1)—Fe(1)—P(2)	84.49 (5)	Fe(1)—N(1)—N(2)	139.1 (4)
P(1)—Fe(1)—N(1)	90.44 (1)	N(1)—N(2)—N(3)	176.9 (6)
P(2)—Fe(1)—N(1)	90.24 (1)		

Data were reduced and Lorentz, polarization and absorption corrections were applied using the TEXSAN system (Molecular Structure Corporation, 1993). The structure was solved by heavy-atom methods and refined by full-matrix least-squares analysis with TEXSAN. One of the ethyl groups [C(5)—C(6)] was found to be disordered over two sites. H atoms, except those on C(5) and C(6), were included at calculated sites with isotropic displacement parameters fixed to those of the parent atom. All other atoms were refined anisotropically. The atomic nomenclature is defined in the ORTEP plot (Johnson, 1965) given in Fig. 1.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1025). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Copper(II) and Nickel(II) Complexes with 3,14-Dimethyl-2,6,13,17-tetraazatricyclo[16.4.0.0^{7,12}]docosane, [M(C₂₀H₄₀N₄)]Cl₂·2H₂O (M = Cu^{II} and Ni^{II})

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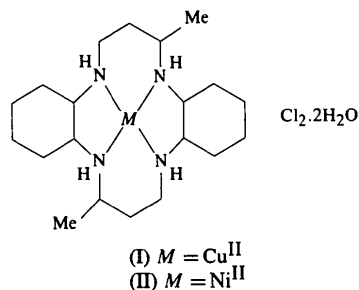
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Abstract

The structures of (3,14-dimethyl-2,6,13,17-tetraazatricyclo[16.4.0.0^{7,12}]docosane-*N,N',N'',N'''*)copper(II) dichloride dihydrate, [Cu(C₂₀H₄₀N₄)]Cl₂·2H₂O, and (3,14-dimethyl-2,6,13,17-tetraazatricyclo[16.4.0.0^{7,12}]docosane-*N,N',N'',N'''*)nickel(II) dichloride dihydrate, [Ni(C₂₀H₄₀N₄)]Cl₂·2H₂O, are presented. Both complexes have an MN₄ square plane involving the four N atoms of the docosane ligand. In the copper complex, water molecules occupy the two axial positions, though the Cu···O distances are longer than the normal coordination ranges. In the nickel complex, the water molecules are displaced too far from the metal coordination sphere to be considered bonded to the Ni atom.

Comment

To our knowledge, this is the first report of the structures of the Cu complex, (I), and the Ni complex, (II), with the 3,14-dimethyl-2,6,13,17-tetraazatricyclo[16.4.0.0^{7,12}]docosane ligand. The ligand was synthesized by previously reported methods (Hay & Lawrence, 1975; Kang, Kweon & Jung, 1991) (see *Experimental*).



In both structures, the metal atom is located on an inversion center. The ligand contains two cyclohexane rings, which have chair conformations in both complexes, and a central ring of 14 atoms. The complexes contain MN₄ square-planar units. Because of the presence of the inversion center, the MN₄ atoms are exactly coplanar in each structure. The Cl⁻ ions in both structures participate in hydrogen bonding (Table 4). A major

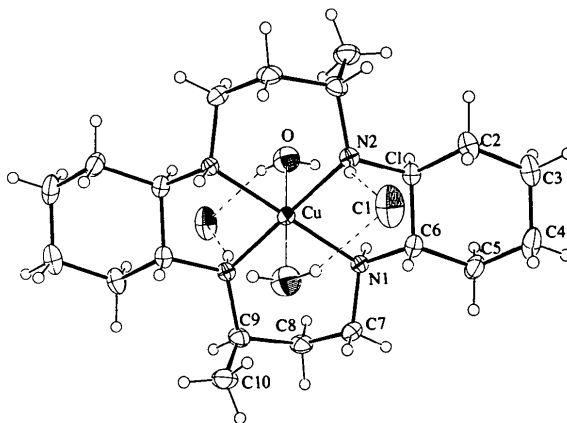


Fig. 1. ORTEP (Johnson, 1976) drawing of complex (I) with the atom-labelling scheme. Displacement ellipsoids are drawn at 40% probability. Dashed lines indicate hydrogen bonds.

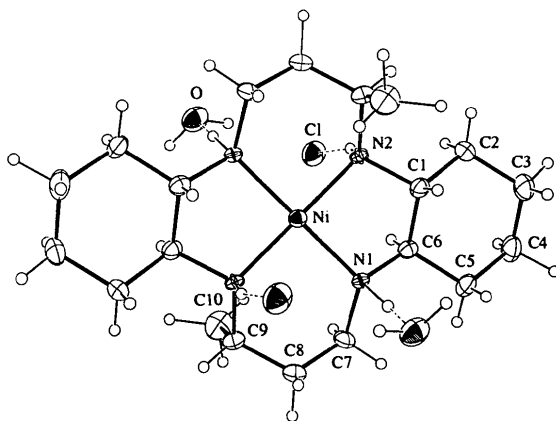


Fig. 2. ORTEP (Johnson, 1976) drawing of complex (II) with the atom-labelling scheme. Displacement ellipsoids are drawn at 40% probability. Dashed lines indicate hydrogen bonds.