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(5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-1,4,8,11-tetraene-*N,N',N'',N'''*)nickel(II) diperchlorate

JACOBO GÓMEZ-LARA,^a ELENA V. BASIUK,^a VLADIMIR A. BASIUK^b AND SIMÓN HERNÁNDEZ-ORTEGA^a

^a*Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior CU, 04510 México DF, Mexico*, and ^b*Instituto de Ciencias Nucleares, Universidad Nacional Autónoma de México, Circuito Exterior CU, A. Postal 70-543, 04510 México DF, Mexico*. E-mail: elenagd@servidor.unam.mx

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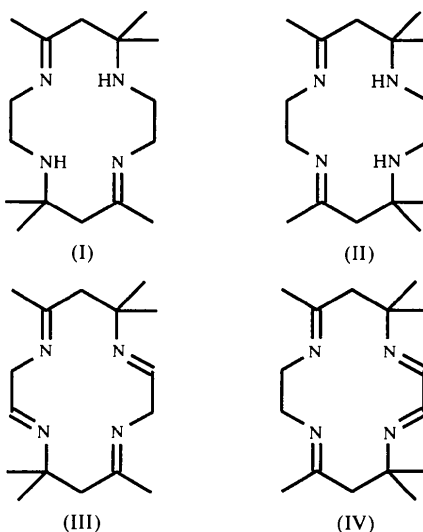
Abstract

In the title compound, [Ni(C₁₆H₂₈N₄)](ClO₄)₂, all the Ni—N distances are approximately equal [1.896 (3)–1.904 (2) Å]. There is no direct interaction between the Ni atoms and the perchlorate ions. Although most C···O interactions are close to or insignificantly less in size than those expected for van der Waals packing, one was found to be 3.105 (7) Å.

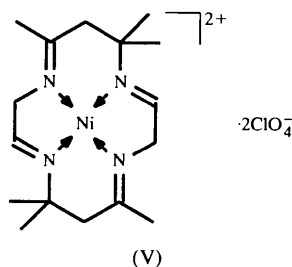
Comment

Tetraaza-macrocyclic compounds derived from condensation of amines (or their metal complexes) with

aliphatic carbonyl compounds (Curtis, 1968) remain classic objects for X-ray structural studies (Hu *et al.*, 1996; Lu *et al.*, 1996; Panneerselvam *et al.*, 1998; Simonov *et al.*, 1998; Wang *et al.*, 1996). The most important representatives, first of all due to their easy preparation, are Ni^{II} complexes with the neutral ligands composed of ethylenediamine and acetone fragments commonly called Me₆trans[14]dieneN₄, (I), and Me₆cis[14]dieneN₄, (II), as well as with the oxidized ligands Me₆trans[14]teteneN₄, (III), and Me₆cis[14]teteneN₄, (IV). While the structures of nickel complexes (I), (II) and (IV) (as perchlorate salts) were reported long ago (Bailey & Maxwell, 1972; Kilbourn *et al.*, 1969; Maxwell & Bailey, 1972), the corresponding complex of (III) has not been characterized.



We present here the X-ray structure determination of the latter compound, (5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1,4,8,11-tetraene-*N,N',N'',N'''*)nickel(II) diperchlorate, (V). All the Ni—N distances in the complex are approximately equal [Ni1—N1 1.904 (2) and Ni1—N5 1.896 (3) Å].



As in the three perchlorate salts studied before, there is no direct interaction between Ni atoms and the perchlorate ions (in the present case, the shortest Ni···O distance was 3.183 (6) Å for Ni1···O2). As a rule, the

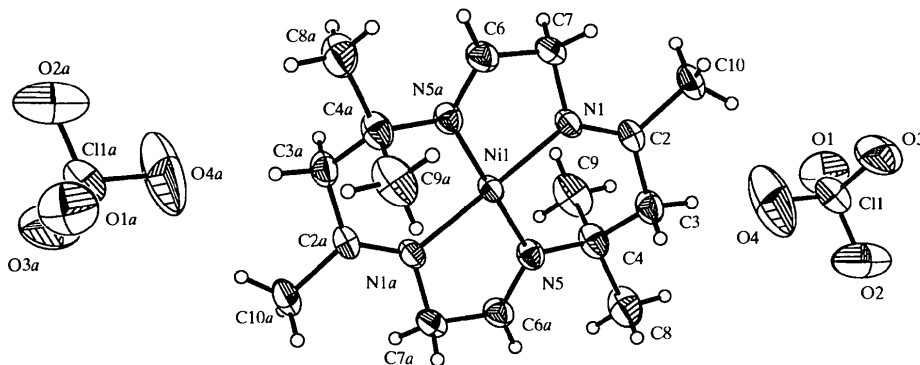


Fig. 1. The molecular structure of (V) showing 40% probability displacement ellipsoids for non-H atoms. H atoms are shown as spheres of arbitrary radii.

C...O interactions are close to or insignificantly less than those expected for van der Waals packing, as in the *cis*-isomer (Maxwell & Bailey, 1972) and in [Ni(Me₆*cis*[14]dieneN₄)] diperchlorate (Kilbourn *et al.*, 1969). The only exception is C6...O3 which was found to be 3.105 (7) Å.

Experimental

Caution: perchlorate salts of metal complexes are potentially explosive and should be handled with care. The title complex was synthesized as described by Curtis (1971). Crystals suitable for X-ray analysis were obtained by slow crystallization from water at room temperature.

Crystal data

[Ni(C₁₆H₂₈N₄)](ClO₄)₂

M_r = 534.035

Triclinic

*P*1̄

a = 6.866 (3) Å

b = 9.101 (4) Å

c = 9.927 (4) Å

α = 100.62 (2)°

β = 90.85 (3)°

γ = 109.34 (2)°

V = 573.4 (4) Å³

Z = 1

D_x = 1.5467 Mg m⁻³

D_m not measured

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 49 reflections

θ = 4.72–24.75°

μ = 1.128 mm⁻¹

T = 293 (2) K

Laminar prism

0.44 × 0.18 × 0.06 mm

Yellow

Data collection

Siemens P4/PC diffractometer

ω/2θ scans

Absorption correction:

analytical, face-indexed

numerical

T_{min} = 0.637, *T_{max}* = 0.956

4100 measured reflections

3334 independent reflections

2475 reflections with

I > 2σ(*I*)

R_{int} = 0.052

θ_{max} = 29.99°

h = -1 → 9

k = -12 → 12

l = -13 → 13

3 standard reflections

every 97 reflections

intensity decay: 1.2%

Refinement

Refinement on *F*²

R[*F*² > 2σ(*F*²)] = 0.056

wR(*F*²) = 0.156

S = 0.943

3334 reflections

142 parameters

H atoms not refined

w = 1/[σ²(*F_o*²) + (0.0950*P*)²]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} < 0.001

Δρ_{max} = 0.905 e Å⁻³

Δρ_{min} = -0.979 e Å⁻³

Extinction correction: none

Scattering factors from

International Tables for

Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Ni1—N5	1.896 (3)	N1—C7	1.472 (4)
Ni1—N5 ⁱ	1.896 (3)	C4—N5	1.498 (4)
Ni1—N1 ⁱ	1.904 (2)	N5—C6 ⁱ	1.275 (4)
Ni1—N1	1.904 (2)	C6—N5 ⁱ	1.275 (4)
N1—C2	1.287 (4)		
N5—Ni1—N5 ⁱ	180.0	N5—Ni1—N1	95.25 (11)
N5—Ni1—N1 ⁱ	84.75 (11)	N5 ⁱ —Ni1—N1	84.75 (11)
N5 ⁱ —Ni1—N1 ⁱ	95.25 (11)	N1 ⁱ —Ni1—N1	180.0

Symmetry code: (i) -*x*, -*y*, -*z*.

H atoms were placed in calculated positions with *U*_{iso} fixed at 0.04 Å².

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXTL-Plus (Siemens, 1990) (direct methods). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997). Molecular graphics: XP in SHELXTL-Plus. Software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1042). Services for accessing these data are described at the back of the journal.

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Cubane tetrameric complexes of copper(I) chloride and bromide with triphenyl phosphite

ROBERT D. PIKE,^a WILLIAM H. STARNES JR^a AND GENE B. CARPENTER^b

^aDepartment of Chemistry, College of William and Mary, Williamsburg, VA 23187, USA, and ^bDepartment of Chemistry, Brown University, Providence, RI 02912, USA.
E-mail: rdpike@facstaff.wm.edu

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Abstract

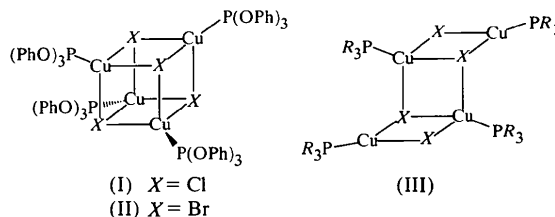
The crystal structures of tetra- μ_3 -chloro-tetrakis[(triphenyl phosphite-*P*)copper(I)], [Cu₄Cl₄(C₁₈H₁₅O₃P)₄], and tetra- μ_3 -bromo-tetrakis[(triphenyl phosphite-*P*)copper(I)], [Cu₄Br₄(C₁₈H₁₅O₃P)₄], are described. Both have distorted 'cubane' Cu₄X₄ cores. Distortion of the cubane structure is reflected in X—Cu—X angles > 90° and Cu—X—Cu angles < 90°, and is more pronounced in the bromide complex.

Comment

We have demonstrated recently that Cu^I-halide-phosphite complexes can induce crosslinking in thermally degrading poly(vinyl chloride) (PVC; Pike *et al.*, 1997). This crosslinking appears to be the result of the reduc-

tive coupling of allylic chloride sites, caused by low-valent Cu centers. Given this activity, Cu^I-phosphite complexes may be of importance as smoke-suppressant additives for PVC. During the course of our study, we prepared a number of complexes with the stoichiometry [CuXL]_n, where X is a halide and L is a phosphite ligand. Although such complexes have long been known (Nishizawa, 1961), no X-ray structural information is available for these species.

We were readily able to prepare crystals of [Cu₄Cl₄(C₁₈H₁₅O₃P)₄], (I), and [Cu₄Br₄(C₁₈H₁₅O₃P)₄], (II). However, the iodide complex, which has a 1:2 Cu:I ratio (Nishizawa, 1961), was not readily crystallizable. Both (I) and (II) proved to be composed of a 'cubane' Cu₄X₄ core, in which each halide bridges three metal atoms and each metal atom is coordinated to a phosphite and three halide ligands. This arrangement is very well known for complexes of Cu^I and Ag^I halides. The cubane core structure has previously been observed for many phosphine complexes, including [MXL]₄ (M = Cu or Ag, X = Cl, Br or I, and L = PPh₃ or PEt₃; Churchill & Kalra, 1974*a,c*; Churchill, DeBoer & Mendak, 1975; Churchill & DeBoer, 1975; Churchill *et al.*, 1976; Teo & Calabrese, 1976*a,b,c*; Barron *et al.*, 1984; Dyason *et al.*, 1985), [CuI(PMePh₂)₄] (Churchill & Rotella, 1977), and [CuBr(P^tBu)₃]₄ (Goel & Beauchamp, 1983). An alternative arrangement of the Cu₄X₄ core, described as a step cluster, (III), is less common and is found for polymorphs of [CuX(PPh₃)₄] (X = Br or I; Churchill & Kalra, 1974*b*; Churchill, DeBoer & Donovan, 1975) and [AgI(PPh₃)₄] (Teo & Calabrese, 1976*c*). The trimesitylphosphine ligand proved sufficiently bulky to produce [CuBr(PMe₃)] as a monomer with two-coordinate Cu^I (Alyea *et al.*, 1985).



In contrast to several previously reported [MXL]₄ series, the triphenylphosphite chloride, (I), and bromide, (II), complexes of Cu^I were not isomorphous. Complex (I) crystallized in the monoclinic space group *P2₁/n* (*Z* = 4) and complex (II) in the trigonal space group *R $\bar{3}$* (*Z* = 6). For complex (II), the atoms Br1, Cu1 and P1 are located on the threefold axis, and only one third of the molecule is independent. As has been observed previously, the cubane core becomes increasingly distorted as the size of the halide ligand increases. Thus, complex (I) shows only slight distortion from cubane geometry; Cl—Cu—Cl bond angles average 94 (3)°, and Cu—Cl—Cu angles average 85 (2)°. Complex (II)