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Monodentate Ligation of Tetracyanonickelate(II): (2-Aminoethanol)[N-(2-aminoethyl)-1,2-ethanediamine][tetracyanonickelato(II)]copper(II)–Water (1/2)†

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Abstract

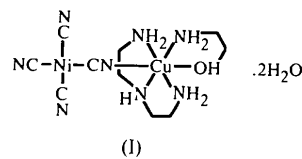
In the title complex, [CuNi(CN)₄(C₄H₁₃N₃)(C₂H₇NO)]·2H₂O, the Cu atom, chelated by a terdentate dien [dien = N-(2-aminoethyl)-1,2-ethanediamine] and a bidentate mea (mea = 2-aminoethanol) ligand, is ligated additionally with [Ni(CN)₄]²⁻ monodentately at the N atom of one CN group; the three other N atoms are free from ligation. This is a rare example of tetracyanonickelate(II) bridging to another coordination centre through only one CN group.

Comment

A tetracyanometallate anion centred by a divalent *d*⁸ transition metal, Ni, Pd or Pt, can behave as a

† Systematic name: (2-aminoethanol)-2κN,2κO-[N-(2-aminoethyl)-1,2-ethanediamine]-2κ³N-μ-cyano-1κC:2κN-tricyano-1κ³C-coppernickel dihydrate.

bridging ligand to other coordination centres via the cyano N atoms, as can *d*¹⁰ cyanometallates such as [Cd(CN)₄]²⁻, [Cu(CN)₄]³⁻ and [Ag(CN)₂]⁻ (Iwamoto, 1996*a,b*). A variety of multidimensional structures have been obtained in which [Ni(CN)₄]²⁻ forms a tetramonodentate cross joint, by using all the N atoms, or a di-monodentate bridge, by using the N atoms of *trans* or *cis* CN groups, to other coordination centres. Recently, a T-1D (T-shaped one-dimensional extension) catenation (Iwamoto, 1996*a,b*), *i.e.* a one-dimensional ladder structure, involving the tri-monodentate [Ni(CN)₄]²⁻ or [Pt(CN)₄]²⁻ moieties using three of the four CN groups to bridge three Eu^{II} atoms successively, has been reported (Knoepfel & Shore, 1996). Another example of T-type three-handed coordination exists for two polymorphs of [Cu(tn)Ni(CN)₄] (tn = 1,3-propanediamine), in which [Ni(CN)₄]²⁻ is linked to three Cu^{II} atoms (Černák, Lipkowski & Hudak, 1996). Thus, four-, three- and two-handed coordination structures with tetracyanonickelate(II) as a bridging ligand have been demonstrated, as is illustrated in Fig. 1. Monodentate ligation has been found in the crystal structure of the title complex, (I).



As shown in Fig. 2, the neutral discrete molecule of (I) is binuclear. One of the coordination centres, the octahedral Cu^{II}, is chelated with the terdentate dien and bidentate mea ligands, N atoms of both ligands being on the equatorial plane; the O atom of the mea is in the axial position. The other side of the axial position is coordinated monodentately by the N1 atom of [Ni(CN)₄]²⁻, leaving three of the CN groups free from coordination. To the authors' knowledge, this is the first case of monodentate ligation of [Ni(CN)₄]²⁻ in a well defined crystal structure.

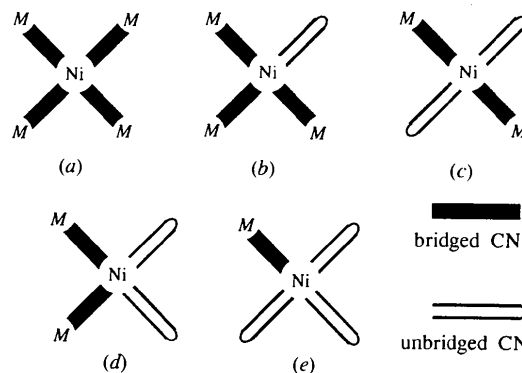


Fig. 1. Coordination modes of square-planar [Ni(CN)₄]²⁻ as a bridging ligand: (a) four-handed, (b) three-handed, (c) two-handed in *trans*, (d) two-handed in *cis*, (e) one-handed.

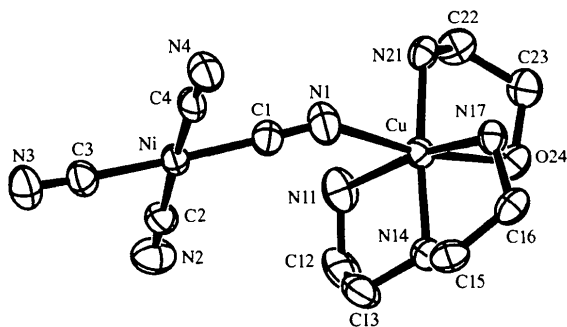


Fig. 2. Coordination structure of the title complex with 50% probability displacement ellipsoids.

The coordination sphere about the octahedral Cu^{II} atom shows a typical Jahn–Teller distortion; it is elongated tetragonally with an axial Cu—O24(me_a) distance of 2.527 (3) Å and a Cu—N1(CN) distance of 2.474 (4) Å, whereas the equatorial Cu—N distances range from 1.992 (4) to 2.053 (4) Å. The bond angles deviate from 90° within the usual range, the largest distortion being 78.0 (1)° for N21(me_a)—Cu—O24(me_a).

Despite the fact that the monodentate [Ni(CN)₄]²⁻ moiety coordinates to Cu^{II} obliquely, with a C1—N1—Cu angle of 143.7 (3)°, its square-planar structure is distorted to some extent, with bond angles that deviate from 90° by about 3° at most; no significant differences are seen in the Ni—C and C—N bond distances within this moiety. Such rigidity of the square-planar configuration is generally seen for [Ni(CN)₄]²⁻ in various bridging structures, regardless of the difference in the mode of bridging coordination (Černák, Dunaj-Jurčo, Melnik, Chomič & Skorsepa, 1988; Iwamoto, 1996*a,b*).

The coordination-free N atoms of the monodentate [Ni(CN)₄]²⁻ moiety appear to be hydrogen bonded to the water molecules of hydration, with distances of 3.060 (5) Å for N2···OW1($\frac{1}{2}-x, \frac{1}{2}+y, -z-\frac{1}{2}$), 2.921 (6) Å for N2···OW2 and 2.844 (5) Å for N3···OW1($x, 1+y, z$); the N4···N14($x, 1+y, z$) distance of 3.037 (6) Å suggests the formation of a hydrogen bond with the imino N atom of dien.

In our experience from more than 200 single-crystal structure analyses, the me_a–citric acid buffer is often appropriate for growing well developed single crystals of multidimensional cyanometallates. However, complexes involving me_a as a ligand crystallize by chance; examples are [Cd(me_a)(daptn){Ni(CN)₄}] (daptn = 1,5-diaminopentane), [Cd(me_a)(dahxn){Ni(CN)₄}].H₂O (dahxn = 1,6-diaminohexane) (Yuge, Nishikiori & Iwamoto, 1996), and [Cd(4-ampy)₂{μ-Ag(CN)₂}₂].[Cd(me_a)(4-ampy){Ag(CN)₂}{μ-Ag(CN)₂}₂] (4-ampy = 4-aminopyridine) (Soma & Iwamoto, 1996). As for the use of the terdentate dien, we have obtained a three-dimensional cage of [Cd₈(CN)₁₉]³⁻ imprisoning two kinds of Werner complex cations, a monomeric

[Cd(dien)₂]²⁺ and a dimeric [Cd₂(CN)₃(dien)₂]⁺, from an aqueous solution containing CdCl₂, K₂[Cd(CN)₄] and dien buffered with citric acid only, in the absence of me_a (Kurihara, Nishikiori & Iwamoto, 1997). In the present case, the chelation of the me_a together with the dien to the octahedral Cu^{II} atom blocks five of the six coordination sites; the blocking is unfavourable for extending a multidimensional structure. Another monodentate ligand is required to accomplish the sixfold coordination. The monodentate ligation of [Ni(CN)₄]²⁻ may be due to the Lewis basicity of the N atom being stronger for Cu^{II} under the present conditions of preparation than that of the water O atom.

Experimental

In the course of systematic investigations of crystal engineering to build up multidimensional structures of multidentate amine–transition metal(II)–tetracyanonickelate(II) complexes, blue column-like crystals of the title complex were obtained from an aqueous solution containing CuSO₄, K₂[Ni(CN)₄] and dien (1:1:1), buffered with citric acid and me_a [dien = *N*-(2-aminoethyl)-1,2-ethanediamine and me_a = 2-aminoethanol]; the analytical results supported the composition.

Crystal data

[CuNi(CN)₄(C₄H₁₃N₃)(C₂H₇NO)].2H₂O

M_r = 426.62

Monoclinic

*P*2₁/*n*

a = 11.097 (5) Å

b = 9.869 (5) Å

c = 17.325 (4) Å

β = 104.90 (2)°

V = 1834 (1) Å³

Z = 4

D_x = 1.546 Mg m⁻³

D_m = 1.54 (1) Mg m⁻³

D_m measured by flotation

Mo *K*α radiation

λ = 0.71069 Å

Cell parameters from 25 reflections

θ = 12.9–18.5°

μ = 2.211 mm⁻¹

T = 293 (2) K

Column

0.50 × 0.25 × 0.25 mm

Blue

Data collection

AFC-5 Rigaku Denki diffractometer

ω/2θ scans

Absorption correction: none

4793 measured reflections

4688 independent reflections

3209 reflections with

F > 3σ(*F*)

*R*_{int} = 0.037

θ_{max} = 27.48°

h = 0 → 14

k = 0 → 12

l = -22 → 21

3 standard reflections

every 150 reflections

intensity decay: 2%

Refinement

Refinement on *F*²

R[*F*² > 2σ(*F*²)] = 0.0433

w*R*(*F*²) = 0.1087

S = 1.102

(Δ/σ)_{max} = 0.100

Δρ_{max} = 0.792 e Å⁻³

Δρ_{min} = -0.719 e Å⁻³

Extinction correction: none

3209 reflections
284 parameters
 $w = 1/[\sigma^2(F_o^2) + (0.0629P)^2 + 0.903P]$
where $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from
*International Tables for
Crystallography* (Vol. C)

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***trans*-[2,6-Diacetylpyridine bis(thiosemi-
carbazone)(1-)]diphenyltin(IV) Chloride**

Table 1. Selected geometric parameters (\AA , $^\circ$)

Cu—N14	1.992 (4)	Ni—C3	1.865 (4)
Cu—N21	2.003 (4)	Ni—C1	1.865 (4)
Cu—N17	2.039 (3)	Ni—C2	1.866 (4)
Cu—N11	2.053 (4)	C1—N1	1.144 (5)
Cu—N1	2.474 (4)	C2—N2	1.151 (6)
Cu—O24	2.527 (3)	C3—N3	1.145 (6)
Ni—C4	1.861 (4)	C4—N4	1.150 (5)
N1—C1—Ni	178.1 (4)	C1—N1—Cu	143.7 (3)

All H atoms, except those belonging to the water molecules and the aminoethanol OH group, were located. Their coordinates and isotropic displacement parameters were refined.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1476). Services for accessing these data are described at the back of the journal.

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Abstract

The chelating properties of the pentadentate ligand 2,6-diacetylpyridine bis(thiosemicarbazone) hydrochloride, H₂daptsc.HCl, have been investigated in a new organotin complex, [PhSnPh(Hdaptsc)]Cl {or [Sn(C₆H₅)₂(C₁₁H₁₄N₇S₂)]Cl}. The structure determination revealed a monocationic complex consisting of a heptacoordinated Sn^{IV} in a distorted pentagonal-bipyramidal geometry, with the thiosemicarbazone derivative acting as a pentadentate species at the equatorial plane and two phenyl groups at *trans* positions. The chloride acts as a counterion. ¹¹⁹Sn Mössbauer measurements showed that the isomer shift and the quadrupole splitting are consistent with structural interpretation.

Comment

The chelating properties of 2,6-diacetylpyridine bis(thiosemicarbazones) have been investigated. Three different coordination modes have been found. In the most common one, the ligand acts as a dianionic η^5 ligand and coordinates to the central metal through two thiol S, two azomethine N and the pyridine N atom. This coordination mode was observed in diphenyl[2,6-diacetylpyridine bis(thiosemicarbazone)]tin(IV) bis(dimethylformamide) solvate (Casas *et al.*, 1994). Spectroscopic and X-ray studies showed that 2,6-diacetylpyridine bis(thiosemicarbazones) can also behave as tetradentate dianionic ligands that form square-planar complexes with Ni^{II}, Cu^{II} and Pd^{II} (El-Toukhy, 1991). In this case, the metal ion is coordinated through the pyridine N, the thiolate S, the azomethine N and the thioimide N atom. The other S atom remains in the thione form and does not coordinate. A third coordination mode was reported for the complex *trans*-chloromethyl[2,6-diacetylpyridine bis(thiosemicarbazone)]tin(IV) chloride methanol solvate in which the Sn^{IV} atom is heptacoordinated and has