INORGANIC COMPOUNDS

Copper–Zinc Oxide Catalysts. VII. Zn(NH$_3$)$_{0.7}$(H$_2$O)$_{0.3}$Cu(CN)$_3$

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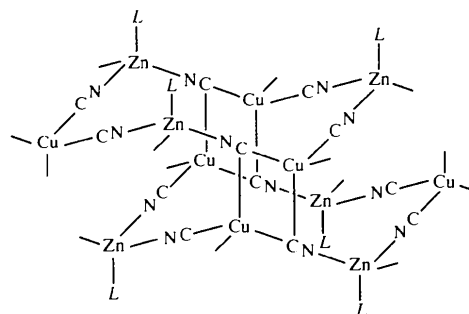
ZCAH [L=(NH$_3$)$_{0.7}$(H$_2$O)$_{0.3}$]

Abstract

The structure of a new Cu–Zn bimetallic compound, poly[ammineaqua-di-μ_2-cyano-μ_3-cyano-copper(I)-zinc(II)], [ZnCu(CN)$_3$(NH$_3$)$_{0.7}$(H$_2$O)$_{0.3}$]$_n$, is built up of infinite double sheets. Each sheet corresponds to a hexagonal network, with Zn and Cu atoms occupying alternate corners of the hexagons and cyano groups forming the edges. The sheets are connected into pairs by weaker Cu—C bonds completing the trigonal pyramidal coordination geometry of copper(I). One of the cyano groups is μ_3-bridging, forming a connection between two Cu and one Zn atom. The Cu—C bonds are not symmetrical [1.966(8) and 2.458(8) Å]. The Zn atom is coordinated by three N-bonded cyano groups and one terminal ligand which consists of a water (30%) and an ammonia molecule (70%).

Comment

An alternative method for the preparation of model catalysts for the methanolization of syngas (CO + H$_2$) is the use of Cu–Zn bimetallic precursors with defined crystal structures and stoichiometries (Porta *et al.*, 1991). In previous papers, we have described the crystal structures of new Cu–Zn compounds, namely, Zn(NH$_3$)$_2$Cu(CN)$_3$ (ZCA), [Zn(en)$_3$]$_6$[Cu$_5$(CN)$_{17}$].nH$_2$O (n = 8.4, ZCE3; Černák *et al.*, 1994) and Zn(NH$_3$)$_3$Cu$_2$(CN)$_4$ (ZC2A; Černák *et al.*, 1996), and have presented a review of the preparation and crystallochemistry of Cu–Zn bimetallic compounds (Černák, 1998). We report here the crystal structure of a new bimetallic compound, Zn(H$_2$O)$_{0.3}$-(NH$_3$)$_{0.7}$Cu(CN)$_3$ (ZCAH), with a Cu:Zn atomic ratio of 1:1. This compound crystallizes from the Zn^{2+}–NH$_3$–[Cu(CN)$_2$]$^-$–H$_2$O system, together with ZCA, in the form of small colorless prisms.

The crystals of ZCAH were separated under a microscope and their composition was checked by FT-IR and CHN analyses. The IR spectrum indicated the presence of both water and ammonia ligands, and bridging cyano groups. The results of CHN analysis gave a value of 3:7 for the water to ammonia ratio.

The main feature of the structure is the occurrence of two-dimensional double sheets running parallel to the x and y axes (Fig. 1). The individual sheets form a puckered hexagonal network. The building block of this network is an 18-membered ring forming a deformed hexagon with a chair-like conformation. The corners of the hexagon are alternatively occupied by Cu and Zn atoms, and the edges are occupied by bridging cyano groups. All edges are shared with neighboring hexagons. The sheets are paired, the second sheet being shifted with regard to the first by half of the hexagon. Two sheets are connected by weaker Cu—C bonds between Cu atoms from the first sheet and C1 atoms from the second. The double sheets are stacked along the z axis through van der Waals contacts, the shortest distances of 3.601(9) Å being for the contacts C1$\cdots$C2($-x$, y, $-z$) and C1$\cdots$C2($-x$, 1 $- y$, $-z$). These van der Waals forces between double sheets result in less efficient packing for the structure of ZCAH (expressed in terms of density; 2.075 Mg m^{-3}) in comparison with the packing of ZCA (2.12 Mg m^{-3}; two-dimensional structure) and even ZC2A (2.10 Mg m^{-3}), which exhibits a one-dimensional structure.

Similar 18-membered hexagonal networks, but formed by Cu^I atoms only (and thus negatively charged) and exhibiting a different spatial arrangement of the sheets, were found in KCu$_2$(CN)$_3$.H$_2$O (Cromer & Larson, 1962), [Me$_2$PhS]Cu$_2$(CN)$_3$ (Černák *et al.*, 1991) and in the superconductor κ-(BEDT-TTF)$_2$-Cu$_2$(CN)$_3$ [BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene; Geiser *et al.*, 1991]; in the last compound, the sheets are essentially planar.

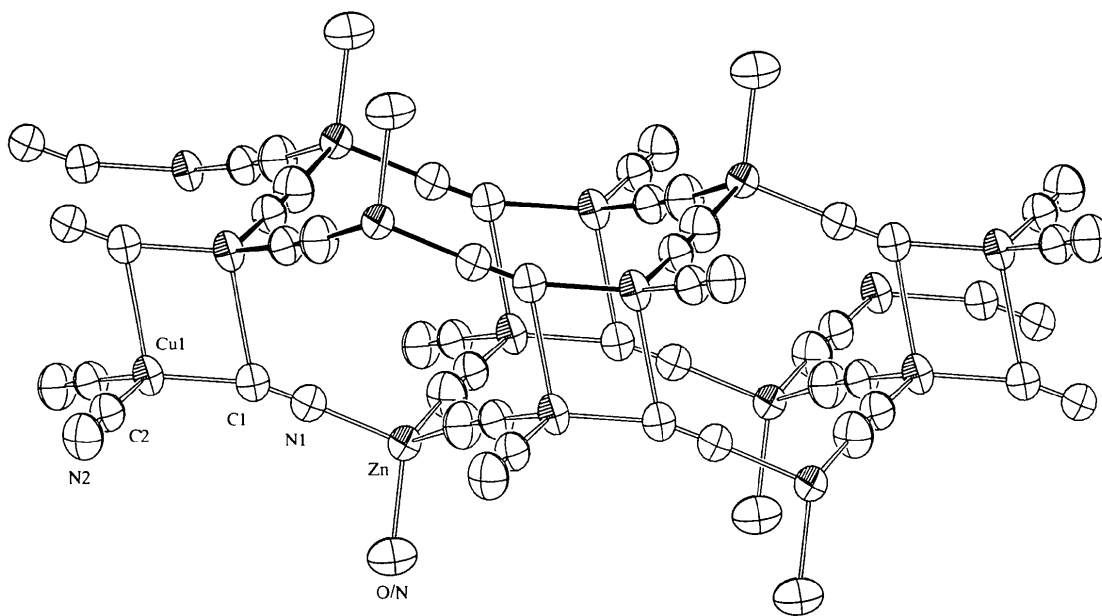The coordination polyhedron around the Cu atom can be described as deformed trigonal pyramidal, with the

Fig. 1. *ZORTEP* (Zsolnai & Pritzkow, 1994) view of the title compound showing its two-dimensional character. The atoms forming a deformed hexagon with a chair-like conformation are shown with solid bonds. The displacement ellipsoids are drawn at the 50% probability level.

C1 atom at a longer apical distance [the Cu atom is displaced from the plane formed by three C atoms by 0.305 (1) Å towards the C1 atom at the apex; the sum of the interbond angles in the assumed plane is 352.7 (6)°]. An alternative way to describe this polyhedron is to consider it as a very deformed tetrahedron. The Zn atom is tetrahedrally coordinated by three bridging cyano groups *via* the nitrogen ends and by one terminal L ligand composed of water and ammonia molecules in the ratio 3:7 (see above). The coordination type of the Zn atom is the same as found in ZCA or ZC2A, but different with regard to the nature of the donor atoms. The Zn—L bonds are directed from the outer side of the double sheet towards the hole of the hexagons of the adjacent double sheet. There are no $L \cdots L$ contacts shorter than 5.368 (7) Å.

An outstanding feature of the title compound is the presence of an unsymmetrical μ_3-cyano group in which the C1 atom in the fragment Cu—C1—N1—Zn forms an additional bond to the neighboring Cu($-x$, $1-y$, $1-z$) atom. The presence of this weaker coordination manifests itself also in a short Cu$\cdots$Cu distance and an important bending of the Cu—C—N angle (Table 2). Such μ_3-cyano groups have, to our knowledge, been described only in the following four cyanocuprate compounds (the first two values are the Cu—C distances, the third corresponds to the Cu$\cdots$Cu distance and the fourth is the Cu—C—N angle): [Me₂PhS]Cu₂(CN)₃ [1.959 (9), 2.419 (8), 2.655 (2) Å and 162.0 (7)°; Černák *et al.*, 1991], Cd-

(H₂O)₃Cu(CN)₃.CH₃CN [2.075 (9) and 2.20 (1) Å, the last two values are not given; Nishikiori & Iwamoto, 1994], CuCN.NH₃ (2.13, 2.09 and 2.42 Å, last value not given; Cromer *et al.*, 1965) and [Cu₅(CN)₆(dmf)₄] (dmf is dimethylformamide) [2.326 (8), 1.972 (7) Å and 160.4 (7)°, the Cu$\cdots$Cu distance is not given; Peng & Liaw, 1986]. Such coordination can be excluded in the case of KCu₂(CN)₃.H₂O (Cromer & Larson, 1962), where the Cu$\cdots$Cu distance is 2.953 (2) Å and the longer Cu$\cdots$C distance is 2.86 (1) Å (calculated values), which is too long to be considered as bonding. An alternative way to describe the coordination around the Cu atoms was presented by Nishikiori & Iwamoto (1994), who describe this anion as [Cu₂(CN)₆]⁴⁻. The shortest Cu$\cdots$Zn distances are Cu$\cdots$Zn($-x$, y, $1-z$) and Cu$\cdots$Zn($-x$, $1-y$, $1-z$) of 4.859 (3) Å.

Experimental

groups [ν(CN): 2154 (ssh), 2136 (vs)]. The results of CHN analysis (found/calculated: C 15.59/16.06, H 1.09/1.21, N 23.26/23.11%) gave a value of 3:7 for the water to ammonia ratio; this ratio was kept constant during the refinement process.

Crystal data

[ZnCu(CN)$_3$(NH$_3$)$_{0.7}$- (H$_2$O)$_{0.3}$]
M_r = 224.30
Monoclinic
$C2/m$
a = 14.346 (7) Å
b = 8.431 (3) Å
c = 6.019 (2) Å
β = 99.48 (5)°
V = 718.1 (5) Å^3
Z = 4
D_x = 2.075 Mg m^{-3}
D_m = 2.07 (1) Mg m^{-3}
D_m measured by flotation in bromoform/chloroform

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 20 reflections
θ = 9.68–13.94°
μ = 6.216 mm^{-1}
T = 293 (2) K
Prism
0.12 × 0.12 × 0.09 mm
Colorless

Data collection

Kuma KM-4 κ-axis diffractometer
ω–2θ scans
Absorption correction: analytical assuming spherical shape (Kuma, 1991)
T_{min} = 0.584, T_{max} = 0.607
1157 measured reflections
1119 independent reflections

744 reflections with $I > 2\sigma(I)$
R_{int} = 0.022
θ_{max} = 30.07°
h = −20 → 0
k = −11 → 0
l = −8 → 8
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.133
S = 1.155
1117 reflections
50 parameters
H atoms not located
$w = 1/[\sigma^2(F_o^2) + (0.0419P)^2 + 2.9700P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = −0.001
$\Delta\rho_{max}$ = 0.555 e Å^{-3}
$\Delta\rho_{min}$ = −0.715 e Å^{-3}
Extinction correction: SHELXL93
Extinction coefficient: 0.0018 (8)
Scattering factors from International Tables for Crystallography (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^ia^j\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
O/N†	−0.3210 (7)	1/2	−0.2477 (13)	0.093 (3)
Cu	0.03823 (6)	1/2	0.3085 (2)	0.0434 (3)
Zn	−0.31151 (5)	1/2	0.09545 (13)	0.0387 (3)
C1	−0.1000 (5)	1/2	0.2856 (13)	0.046 (2)
N1	−0.1771 (5)	1/2	0.2205 (11)	0.052 (2)
C2	0.0966 (4)	0.6973 (7)	0.2436 (9)	0.0461 (11)
N2	0.1306 (4)	0.8108 (7)	0.1972 (9)	0.0602 (13)

† Site occupancies: O 0.3 and N 0.7.

Table 2. *Selected geometric parameters (Å, °)*

O/N—Zn	2.047 (8)	Zn—N1	1.951 (7)
Cu—C2	1.931 (6)	C1—N1	1.111 (10)
Cu—C1	1.966 (8)	C2—N2	1.129 (7)
Cu—C1^i	2.458 (8)	N2—Zn^{ii}	1.943 (5)
Cu···Cu^i	2.711 (2)		
C2—Cu—C2^{iii}	118.9 (3)	N2^{iv}—Zn—O/N	110.9 (2)
C2—Cu—C1	116.9 (2)	N1—Zn—O/N	106.7 (4)
C1—Cu—C1^i	105.3 (3)	N1—C1—Cu	163.6 (7)
C2—Cu···Cu^i	114.9 (2)	Cu—C1—Cu^i	74.7 (3)
N2^{iv}—Zn—N2^v	110.3 (3)	C1—N1—Zn	178.0 (7)
N2^{iv}—Zn—N1	109.0 (2)	N2—C2—Cu	177.3 (5)
N2^{iv}—Zn—O/N	110.9 (2)	C2—N2—Zn^{ii}	175.8 (5)

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $\frac{1}{2}+x, \frac{1}{2}+y, z$; (iii) $x, 1-y, z$; (iv) $x-\frac{1}{2}, y-\frac{1}{2}, z$; (v) $x-\frac{1}{2}, \frac{3}{2}-y, z$.

The analytical absorption correction assumed a spherical shape and used the DATPROC9 program included in the KM-4 software (Kuma, 1991). H atoms of the disordered water and ammonia molecules were not included in the refinement.

Data collection: KM-4 software (Kuma, 1991). Cell refinement: KM-4 software. Data reduction: KM-4 software. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: ZORTEP (Zsolnai & Pritzkow, 1994). Software used to prepare material for publication: SHELXL93. Geometrical analysis: PARST (Nardelli, 1983). All calculations were performed on a PC486 computer.

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