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Bis(2,2'-bipyridine-*N,N'*)(isocyanato-*N*)-copper(II) Tricyanomethanide

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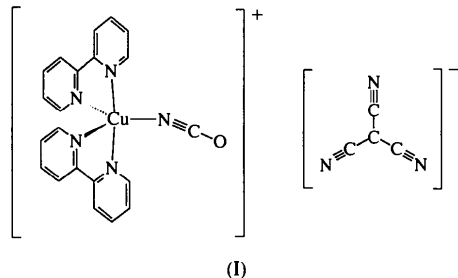
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Abstract

The crystal structure of $[\text{Cu}(\text{NCO})(\text{C}_{10}\text{H}_8\text{N}_2)_2][\text{C}(\text{CN})_3]$ is formed by discrete $[\text{Cu}(\text{bipy})_2(\text{NCO})]^+$ cations and $[\text{C}(\text{CN})_3]^-$ anions (bipy is 2,2'-bipyridine). The coordination polyhedron of the Cu^{II} atom is a distorted trigonal bipyramid with a CuN_5 chromophore.

Comment

In previous papers, we have described structures of compounds containing $[\text{Cu}(\text{phen})_2(\text{X})]^+$ cations [phen is 1,10-phenanthroline and X is a pseudohalogenide anion, *i.e.* CN^- , NCS^- or $\text{N}(\text{CN})_2^-$] and $[\text{C}(\text{CN})_3]^-$ anions (Potočnák *et al.*, 1996*a,b,c*). Our attempts to prepare a similar compound with $\text{X} = \text{NCO}^-$ have always resulted in blue needles of $[\text{Cu}(\text{phen})(\text{NCO})_2]$, the structure of which is already known (Jin *et al.*, 1991). On the other hand, replacement of phenanthroline with the 2,2'-bipyridine ligand yields $[\text{Cu}(\text{bipy})_2(\text{NCO})][\text{C}(\text{CN})_3]$, (I), the preparation and crystal structure of which are presented here and compared with related compounds containing the phenanthroline ligand.



The labeling scheme of one formula unit is shown in Fig. 1. The coordination polyhedron around the Cu atom is a distorted trigonal bipyramid. The Cu atom is five-coordinated by four N atoms of the two bipy molecules and one N atom (in the equatorial plane) of the NCO^- ligand. The tcm^- anion [tcm^- is $\text{C}(\text{CN})_3^-$] does not enter the inner coordination sphere. The two out-of-plane Cu—N20 and Cu—N40 bonds in (I) have similar values [2.003 (3) and 1.983 (3) Å, respectively], and are almost collinear [N20—Cu—N40 171.64 (13)°]. The two in-plane Cu—N bonds (Cu—N10 and Cu—N30) have different values [2.158 (3) and 2.054 (3) Å, respectively] and they are longer on average than the out-of-plane Cu—N distances by 0.106 Å. The third in-plane Cu—N5 (N from the NCO^- ligand) bond of 1.949 (4) Å is the shortest bond in the coordination polyhedron. The out-of-plane angles lie within the range 78.26 (13)–96.32 (12)°. All mentioned values of bond distances and angles are comparable with those of the previously published compounds containing phen.

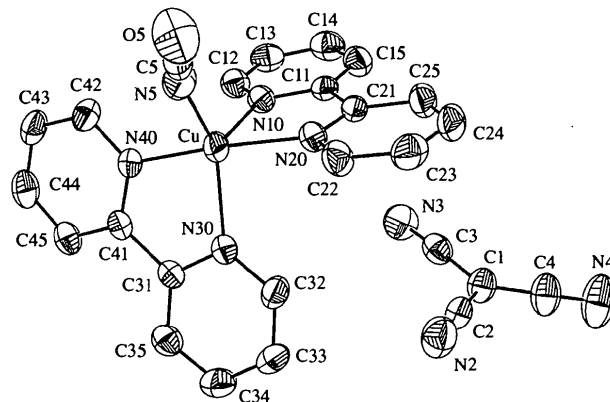


Fig. 1. ORTEP (Johnson, 1965) drawing of the formula unit and labeling of atoms. Displacement ellipsoids are plotted at the 40% probability level.

The bond angles in the equatorial plane of (I) differ considerably from the ideal trigonal angle of 120°, with one large angle of 141.7 (2)° ($\alpha_1 = \text{N5—Cu—N30}$) and two small angles of 114.54 (14)° ($\alpha_2 = \text{N5—Cu—N10}$) and 103.78 (12)° ($\alpha_3 = \text{N30—Cu—N10}$). Thus, the angle α_3 is narrower than the ideal angle of 120° by 16.22° and there is a difference of 27.16° between α_1 and α_2 . According to the criteria of Harrison & Hathaway (1980), the coordination polyhedron around the Cu atom can be best described as distorted trigonal bipyramidal with the square-pyramidal distortion shown by the elongated Cu—N10 equatorial bond. On the other hand, according to the values of the angles α_1 , α_2 and α_3 for pentacoordinated compounds with two phen molecules, their coordination polyhedra can be best described as trigonal bipyramidal with near C_{2v} symmetry. The sum of the bond angles in the equatorial

plane of the title compound (360.02°) indicates coplanarity of the Cu atom with the three equatorial atoms [the deviation of the Cu atom from the N5, N10, N30 plane is 0.000 (2) Å].

Owing to steric considerations in the trigonal-bipyramidal polyhedron, the N atoms of the bipy molecules are coordinated both in equatorial and axial positions. Both bipy molecules are nearly planar [the largest deviation of atoms from the mean planes is 0.088 (5) Å]. The mean planes of the two bipy molecules are inclined at 104.69 (8)° with respect to one another. The aromatic bond distances of both bipy molecules are normal and range from 1.324 (5) to 1.344 (4) Å for N—C bonds, and from 1.350 (7) to 1.393 (5) Å for C—C bonds, single C—C bonds being 1.474 (5) and 1.492 (5) Å. The values of the bond angles within each pyridine ring of both bipy molecules range from 117.4 (4) to 123.0 (4)°, while the values of angles around the C—C bond between the two pyridine rings lie in a somewhat larger range.

The bonding mode of the almost linear isocyanato anion [N5—C5—O5 176.8 (5)°] can be considered as angular [Cu—N5—C5 146.3 (4)°]. Both the bond distances [N5—C5 1.150 (5) and C5—O5 1.192 (5) Å] and angles in the isocyanato anion correspond to the values found for the bridging isocyanato anion in [Cu(phen)(NCO)₂] (Jin *et al.*, 1991).

The tcm⁻ anion is almost planar [the largest deviation of atoms from the mean plane is 0.016 (6) Å]. The mode of bonding in the tcm⁻ anion can be described as a largely delocalized π-bonding system (Golub *et al.*, 1986). According to this assumption, the C—C lengths around the central C1 atom have similar values and they are considerably shorter than single C_{sp²}—C_{sp} bonds (1.440 Å). Although the triple C≡N bond lengths are the same within 2σ, contrary to the above assumption, they are slightly shorter than normal C≡N triple-bond lengths (1.153 Å). The angles around the central C atom are close to the ideal value of 120°, while the C1—Cn≡Nn (n = 2, 3, 4) angles are almost linear.

Experimental

Crystals of (I) were prepared by mixing 10 ml of a 0.1 M water solution of Cu(NO₃)₂ with 20 ml of a 0.1 M ethanol solution of bipyridine, followed by addition of 10 ml of a 0.1 M water-ethanol (1:1) solution of KNCO and 10 ml of a 0.15 M water-ethanol (1:1) solution of KC(CN)₃. The resulting blue precipitate was dissolved by adding 0.3 ml of concentrated ammonia solution. Turquoise crystals of the title complex appeared over a period of several days.

Crystal data

[Cu(NCO)(C₁₀H₈N₂)₂]-
(C₄N₃)
M_r = 508.00
Triclinic
P $\bar{1}$

Mo Kα radiation
λ = 0.71073 Å
Cell parameters from 17
reflections
θ = 4.16–11.26°

a = 8.955 (4) Å
b = 9.702 (5) Å
c = 14.003 (5) Å
α = 84.72 (3)°
β = 85.00 (3)°
γ = 68.74 (3)°
V = 1127.1 (9) Å³
Z = 2
D_x = 1.497 Mg m⁻³
D_m = 1.484 (1) Mg m⁻³
D_m measured by flotation in
CCl₄/benzene

μ = 1.006 mm⁻¹
T = 293 (2) K
Prism
0.40 × 0.20 × 0.15 mm
Turquoise

Data collection

Syntex P2₁ diffractometer
θ/2θ scans
Absorption correction:
ψ scan (North *et al.*,
1968)
T_{min} = 0.703, T_{max} = 0.860
4337 measured reflections
4337 independent reflections

1751 reflections with
I > 2σ(I)
θ_{max} = 27.56°
h = 0 → 11
k = -11 → 12
l = -17 → 18
3 standard reflections
every 100 reflections
intensity decay: <3%

Refinement

Refinement on F²
R[F² > 2σ(F²)] = 0.033
wR(F²) = 0.070
S = 0.691
4336 reflections
380 parameters
All H atoms refined
w = 1/[σ²(F_o²) + (0.0573P)²]
where P = (F_o² + 2F_c²)/3

(Δ/σ)_{max} = 0.003
Δρ_{max} = 0.150 e Å⁻³
Δρ_{min} = -0.200 e Å⁻³
Extinction correction: none
Scattering factors from
International Tables for
Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Cu—N5	1.949 (4)	C1—C2	1.390 (6)
Cu—N40	1.983 (3)	C1—C4	1.386 (7)
Cu—N20	2.003 (3)	C1—C3	1.416 (6)
Cu—N30	2.054 (3)	N2—C2	1.142 (5)
Cu—N10	2.158 (3)	N4—C4	1.138 (6)
N5—C5	1.150 (5)	N3—C3	1.145 (5)
C5—O5	1.192 (5)		
N5—Cu—N40	95.08 (14)	N30—Cu—N10	103.78 (12)
N5—Cu—N20	92.98 (14)	C5—N5—Cu	146.3 (4)
N40—Cu—N20	171.64 (13)	N5—C5—O5	176.8 (5)
N5—Cu—N30	141.7 (2)	C2—C1—C4	120.7 (4)
N40—Cu—N30	80.22 (13)	C2—C1—C3	117.5 (4)
N20—Cu—N30	94.79 (12)	C4—C1—C3	121.7 (4)
N5—Cu—N10	114.54 (14)	N2—C2—C1	179.5 (4)
N40—Cu—N10	96.32 (12)	N4—C4—C1	177.3 (5)
N20—Cu—N10	78.26 (13)	N3—C3—C1	176.7 (5)

Intensities were corrected for Lorentz and polarization factors using XP21 (Pavelčík, 1993). The structure was solved by direct methods with SHELXS86 (Sheldrick, 1990) and subsequent Fourier syntheses using SHELXL93 (Sheldrick, 1993). Anisotropic displacement parameters were refined for all non-H atoms. All H atoms were located from the difference Fourier map and refined with free isotropic displacement parameters. Geometrical analysis was performed using PARST (Nardelli, 1983) and SHELXL93. ORTEP (Johnson, 1965) was employed to produce the figure.

Data collection: Syntex P2₁ software. Cell refinement: Syntex P2₁ software. Software used to prepare material for publication: SHELXL93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1256). Services for accessing these data are described at the back of the journal.

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Diphenylzirconocene

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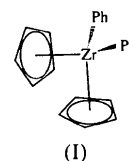
Abstract

The title compound, $[\text{Zr}(\text{C}_5\text{H}_5)_2(\text{C}_6\text{H}_5)_2]$, has two cyclopentadienyl and two phenyl ligands arranged in a distorted tetrahedral geometry around the Zr atom. Steric interactions produce an opening of the Cp—Zr—Cp angle to $131.7(1)^\circ$ and a tilting of both phenyl rings in their own planes about the Zr—C bonds by several degrees.

Comment

Since the discovery by Sinn *et al.* (1980) that the zirconocene dichloride/methylaluminumoxane system was effective as a homogeneous Ziegler–Natta catalyst, there has been considerable research into zirconocene derivatives as polymerization catalysts. Structural analysis of these zirconocenes may provide important clues to the mechanism of polymerization, as well as increasing our knowledge of the structural chemistry of organozirconium compounds.

One of the aims of our current research is to synthesize a mixed lithium–zirconium cluster. Diphenylzirconocene, (I), was chosen as one of the starting materials in the attempted preparation of such a cluster. It was first prepared by Samuel & Rausch (1973) as a white solid, which is stable in air for short periods of time, but is unstable at elevated temperatures, decomposing at 413 K. We report here the previously unknown crystal structure of diphenylzirconocene.



Considering the two cyclopentadienyl (Cp) ligands as occupying one coordination site each, the coordination geometry of zirconium is a rather distorted tetrahedron, with the angle enclosed by the two Cp ligands opened up to $131.7(1)^\circ$ and all the other angles reduced from the ideal value of 109.5° . A search of the Cambridge Structural Database (Allen & Kennard, 1993) reveals a large number of Cp_2ZrX_2 molecular structures, including those with substituted Cp ligands. Of these, 16 have monodentate carbon ligands X (alkyl, alkenyl, alkynyl, aryl or carbonyl) and no constraint on coordination geometry from linking of the Cp ligands through their substituents. The X—Zr—X angle varies widely, between 86.8 [for dicarbonylbis(indenyl)zirconium; Rausch *et al.*, 1987] and 131.3° (for a mixed alkyl–alkenyl complex; Hey-Hawkins & Lindenberg, 1992), while the range of Cp—Zr—Cp angles is much smaller, 126.9 – 145.0° . These variations appear to have mainly steric origins. The Zr—Cp and Zr—C(Ph) distances in diphenylzirconocene lie well within the ranges observed for these other complexes.

The dihedral angle between the two Cp rings is $52.1(2)^\circ$, and that between the two phenyl rings is also $52.1(2)^\circ$. Both phenyl substituents show a distortion from regular hexagonal geometry, with a reduced C—C—C angle at the *ipso*-C atom, and each is tilted within its own plane relative to the Zr—C bond, so that one Zr—C—C angle is markedly larger than the other, probably also to reduce steric interactions. There are no notably short intermolecular contacts. Highly