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Acta Cryst. (1997). C**53**, 703–705

trans-Bis(cyanamidonitrato-*N*:*O*)bis(imidazole-N^3)copper(II), $[Cu(CN_3O_2)_2(C_3H_4N_2)_2]$

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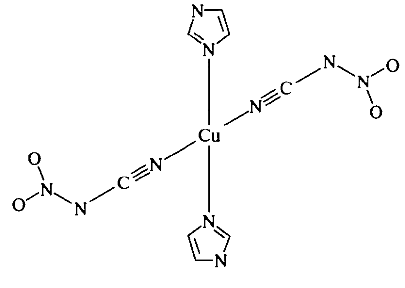
(*Received 22 October 1996; accepted 22 January 1997*)

Abstract

The structure of the title compound consists of one-dimensional polymeric chains extending along the **c** direction. They are formed by linking $[Cu(NCNNO_2)_2(iz)_2]$ (iz is imidazole) units together. The cyanamidonitrate anions act as bidentate bridging ligands, with a short Cu—N(nitrile) bond of 2.011 (2) Å in the equatorial plane and a long axial Cu—O bond of 2.687 (3) Å. The Cu atom is located on a centre of symmetry and is pseudo-octahedrally coordinated by two *trans* N(imidazole) atoms [Cu—N 1.936 (2) Å] and two nitrile N atoms, and by two axial O atoms from cyanamidonitrate ligands.

Comment

Non-linear pseudo-halides with different donor atoms are potentially polydentate ligands. In the case of complexes of the MX_2L_2 type (where M = Cu^{II}, Ni^{II}, Co^{II}; X = $N(CN)_2$, $C(CN)_3$, $ONC(CN)_2$; L is a neutral ligand of pyrazole or imidazole type), it is highly probable that the anionic ligand X has a bidentate bridging function, as the coordination number of the central atom is usually six. The metal–ligand bond lengths are approximately equivalent in coordination compounds with bidentate bridging dicyanamide and tricyanomethanide, such as $[Ni\{N(CN)_2\}_2(4\text{-meiz})_2]$ (meiz is methylimidazole) (Kožíšek & Hvastijová, 1997) or $[Co\{C(CN)_3\}_2(2\text{-meiz})_2]$ (Hvastijová, Kožíšek, Kohout, Jäger & Fuess, 1995). On the other hand, in $[Cu\{C(CN)_3\}(pyrazole)_4][C(CN)_3]$ or in $[Cu\{C(CN)_3\}_2(pyrazole)_3]$ (Kožíšek, Hvastijová, Kohout, Mroziński & Köhler, 1991), these bond lengths are quite different. The cyanamidonitrate anion, NO_2NCN^-, contains three potential donor atoms, *i.e.* amide and nitrile N atoms and an O atom. It is preferentially coordinated through the nitrile N atom in, for example, $[Cu(NCNNO_2)_2(1\text{-methylimidazole})_4]$ (Kožíšek & Hvastijová, 1997). In $[(CH_3)_3Sn(NCNNO_2)]$ (Jäger, Tretner, Biedermann & Hartung, 1997*a*), the cyanamidonitrate is bonded in a bidentate bridging manner through the nitrile and amide N atoms. The same coordination mode is observed for the Cu^I and the Ag^I complexes of the type $[M(NCNNO_2)(PPh_3)_2]_2$ (Jäger, Tretner, Biedermann & Hartung, 1997*b*). It was therefore of interest to investigate the bonding in the title complex, (I).



(I)

X-ray analysis confirms the coordination number to be six for the central atom and the bidentate bridging function of the cyanamidonitrato ligand. The bridging mode of cyanamidonitrate through the nitrile N and nitrate O atoms observed here is preferred to that found by Jäger *et al.* (1996*a*,*b*) in Sn, Cu^I and Ag^I complexes.

Acta Crystallographica Section C
ISSN 0108-2701 © 1997

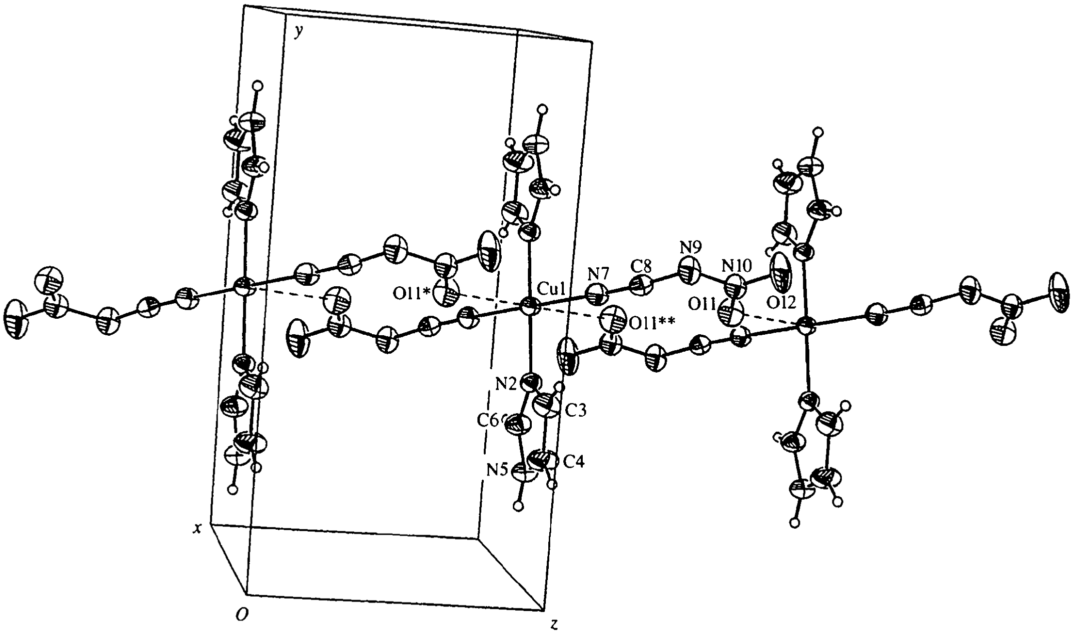


Fig. 1. The crystal structure of the title compound, with displacement ellipsoids given at 50% probability (one-dimensional chains in the **z** direction).

Experimental

For the preparation of $[Cu(NCNNO_2)_2(iz)_2]$, a solution of $Cu(NO_3)_2$ (2.0 mmol) in 4 ml water was mixed with a solution of $KNCNNO_2$ (4.0 mmol) in 5 ml water and with a solution of imidazole (4.0 mmol) in 10 ml methanol. From this system, blue crystals were isolated after a few days.

Crystal data

$[Cu(CN_3O_2)_2(C_3H_4N_2)_2]$
$M_r = 371.76$
Monoclinic
$P2_1/c$
$a = 6.797$ (2) Å
$b = 13.558$ (6) Å
$c = 7.217$ (2) Å
$\beta = 96.58$ (3)°
$V = 660.7$ (4) Å^3
$Z = 2$
$D_x = 1.869$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 21 reflections
$\theta = 5.0$–18.4°
$\mu = 1.696$ mm^{-1}
$T = 293$ (2) K
Block
0.35 × 0.25 × 0.20 mm
Green–blue

Data collection

Syntex $P2_1$ diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical *via* ψ scan (North, Phillips & Mathews, 1968)
$T_{min} = 0.562$, $T_{max} = 0.712$
2363 measured reflections
1937 independent reflections

1227 reflections with $I > 2\sigma(I)$
$R_{int} = 0.018$
$\theta_{max} = 32.01°$
$h = -10 \rightarrow 10$
$k = -19 \rightarrow 19$
$l = 0 \rightarrow 9$
2 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0359$
$wR(F^2) = 0.1020$
$S = 0.975$
1937 reflections
107 parameters
H atoms riding on C or N atoms
$w = 1/[\sigma^2(F_o^2) + (0.0525P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.03$

$\Delta\rho_{max} = 0.83$ e Å^{-3}
$\Delta\rho_{min} = -0.45$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.009 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

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

	x	y	z	U_{eq}
Cu1	1/2	1/2	0	0.02531 (15)
N2	0.4019 (3)	0.3659 (2)	−0.0008 (3)	0.0271 (5)
C3	0.4973 (4)	0.2789 (2)	−0.0093 (5)	0.0350 (6)
C4	0.3790 (4)	0.2030 (2)	−0.0032 (4)	0.0384 (7)
N5	0.2098 (4)	0.2440 (2)	0.0116 (4)	0.0452 (7)
C6	0.2285 (4)	0.3414 (2)	0.0134 (5)	0.0384 (7)
N7	0.3053 (3)	0.5434 (2)	0.1734 (4)	0.0318 (5)
C8	0.2286 (3)	0.5708 (2)	0.3000 (4)	0.0278 (6)
N9	0.1258 (3)	0.6099 (2)	0.4287 (4)	0.0360 (6)
N10	0.1844 (3)	0.5830 (2)	0.6158 (4)	0.0330 (5)
O11	0.3172 (3)	0.5269 (2)	0.6535 (3)	0.0433 (5)
O12	0.1007 (3)	0.6198 (2)	0.7447 (3)	0.0603 (8)

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

Cu1—N2	1.936 (2)	N5—C6	1.326 (4)
Cu1—N7	2.011 (2)	N7—C8	1.163 (4)
Cu1—O11^i	2.687 (3)	C8—N9	1.335 (4)
N2—C6	1.241 (3)	N9—N10	1.411 (3)

N2—C3	1.351 (3)	N10—O11	1.188 (3)
C3—C4	1.310 (4)	N10—O12	1.249 (3)
C4—N5	1.292 (4)		
N2—Cu1—N7	91.5 (1)	C8—N9—N10	116.8 (2)
N2—Cu1—O11^{i}	90.1 (1)	O11—N10—O12	119.0 (3)
N7—Cu1—O11^{i}	105.8 (1)	O11—N10—N9	120.6 (2)
C8—N7—Cu1	165.5 (2)	N10—O11—Cu1^{ii}	123.9 (2)
N7—C8—N9	172.3 (3)		

Symmetry codes: (i) $x, y, z - 1$; (ii) $x, y, 1 + z$.

Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990) (Patterson methods). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1971).

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: MU1302). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). C**53**, 705–707

Λ-Tris(1,10-phenanthroline-*N*,*N*′)-ruthenium(II) Bis(hexafluorophosphate)–Acetonitrile–Diethyl Ether (1/1/0.5)

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(Received 18 April 1996; accepted 22 January 1997)

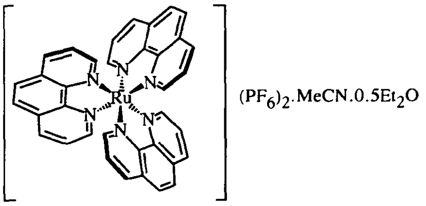
Abstract

The title compound was obtained from a solution of the resolved compound as an acetonitrile 0.5-diethyl ether solvate, $[Ru(C_{12}H_8N_2)_3](PF_6)_2.CH_3CN.0.5(CH_3CH_2)_2O$. The cations possess idealized D_3 symmetry with three bidentate phenanthroline ligands arranged about each Ru^{II} center in a propeller-like fashion. Assignment of the appropriate polar space group corroborates the absolute configuration of the compound with chemical and circular dichroism data.

Comment

The chemistry of tris-chelated compounds of ruthenium(II) with bidentate nitrogen-donor ligands such as 1,10-phenanthroline (phen) and 2,2′-bipyridine (bpy) has been studied for many years (Seddon & Seddon, 1984). Interest in these compounds continues unabated, due largely to their rich photophysical properties (Fox & Channon, 1988) and the interaction of these chiral transition metal complexes with DNA (Hiort, Lincoln & Nordén, 1993; Barton, Goldberg, Kumar & Turro, 1986). It is surprising, therefore, that while a structural report exists for $Ru(bpy)_3^{2+}$ (Rillema, Jones & Levy, 1979), no analogous data have been reported for $Ru(phen)_3^{2+}$, nor has the absolute configuration of one of its enantiomers been confirmed until now.

There are two molecules in the asymmetric unit of the title compound, (I). Each Ru center exists in a distorted octahedral environment, as demonstrated by the values of the 30 N—Ru—N angles, all of which would have values of either 90 or 180° in an ideal octahedral arrangement. The 12 independent Ru—N bond lengths range from 2.058 (8) to 2.082 (6) Å, with an average value of 2.067 Å. These values compare well with the average Ru—N_{bpy} bond length of 2.056 (6) Å in $Ru(bpy)_3(PF_6)_2$ and the calculated Ru—N_{phen} bond length of 2.054 Å in $Ru(phen)_3^{2+}$ (Lincoln, Broo & Nordén, 1996). The C—C bond lengths in the cations range from 1.33 to 1.46 Å, with an average e.s.d. of 0.01 Å. The idealized D_3 symmetry of the molecule is evidenced by the angles formed by the least-squares planes of the three ligands of each cation, which are approximately 80, 86 and 90° for those associated with Ru1, and 86, 90 and 87° for those associated with Ru2. For each cation, the ligands form a 'pitch' angle with the pseudo-threefold axis of the molecule of between 35.0 and 37.4°.



(I)

Most importantly, successful assignment of the absolute structure of this compound permits unambiguous assignment of the crystal used for this investigation