Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS
ISSN 2056-9890

Synthesis, crystal structure and properties of bis(isoselenocyanato-κN)tetrakis(4-methoxypyridine-κN)cobalt(II)

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Received 8 February 2023
Accepted 15 February 2023

Edited by S. Parkin, University of Kentucky, USA

Keywords: crystal structure; nickel selenocyanate; discrete complex; thermal properties.

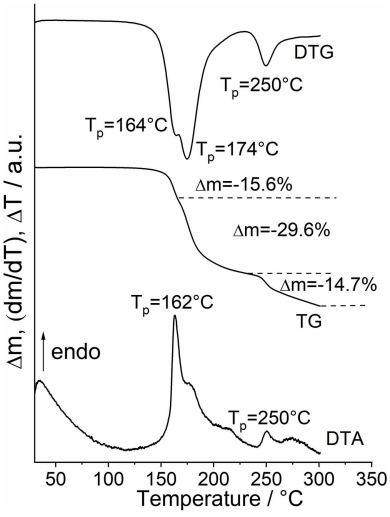
CCDC reference: 2242297

Supporting information: this article has supporting information at journals.iucr.org/e

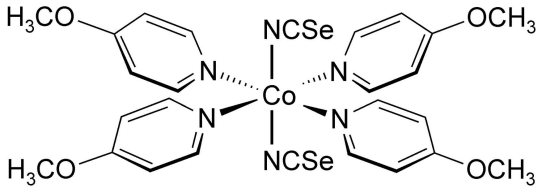
Reaction of $CoCl_2 \cdot 6H_2O$ with KNCSe and 4-methoxypyridine in water led to the formation of the title compound, $[Co(NCSe)_2(C_6H_7NO)_4]$ or $Co(NCSe)_2$(4-methoxypyridine)$_2$, which was characterized by single-crystal X-ray diffraction. Its asymmetric unit consists of one crystallographically independent Co cation, two selenocyanate anions and four 4-methoxypyridine coligands in general positions. In the crystal structure, the cobalt cations are sixfold coordinated by two terminal N-bonded selenocyanate anions and four 4-methoxypyridine coligands within a slightly distorted octahedral coordination. Between the complexes, weak C—H···Se interactions are found. IR spectroscopic investigations revealed that the CN stretching vibration of the anionic ligands is observed at 2068 cm^{-1}, which is in agreement with the presence of only terminally coordinated selenocyanate anions. PXRD measurements prove that a pure compound was obtained. Differential thermoanalysis coupled to thermogravimetry (DTA-TG) at different heating rates shows that the TG curves are poorly resolved. PXRD measurements of the residue obtained by a TG measurement prove that an amorphous compound was obtained.

1. Chemical context

Coordination compounds based on transition-metal thiocyanates show versatile structural behavior (Buckingham, 1994; Barnett *et al.*, 2002; Werner *et al.*, 2015) and promising magnetic properties, because this ligand is able to mediate reasonable magnetic exchange (Barasiński *et al.*, 2010; Palion-Gazda *et al.*, 2015; Mousavi *et al.*, 2020). In this context, compounds based on $Co(NCS)_2$ are of special interest because they can show interesting magnetic behavior, such as, for example, slow relaxations of the magnetization, which is indicative of single-chain magnetism (Lescouëzec *et al.*, 2005; Sun *et al.*, 2010; Dhers *et al.*, 2015). For the synthesis of such compounds, the Co^{II} cations must be linked *via* the anionic ligands into mono-periodic or di-periodic networks. Compounds with di-periodicity are rare; the majority of compounds being mono-periodic, in which the Co^{II} cations are octahedrally coordinated and linked into chains by pairs of anionic ligands (Guang *et al.*, 2007; Shi *et al.*, 2007; Shurdha *et al.*, 2013; Prananto *et al.*, 2017). If the chains are linear, ferromagnetic ordering (Werner *et al.*, 2014) or single-chain magnet behavior (Mautner *et al.*, 2018) is observed and if they are corrugated or exhibit an alternating Co coordination, the magnetic exchange is weak or completely suppressed (Dockum *et al.*, 1983; Böhme *et al.*, 2020, 2022). All this is well investigated for $Co(NCS)_2$ compounds but not much is known



for compounds based on $Co(NCSe)_2$, because only two compounds with μ-1,3-bridging selenocyanate anions are reported in the literature (Boeckmann *et al.*, 2011; Wöhlert *et al.*, 2012; Neumann *et al.*, 2019). First results indicate that they behave in a similar manner to their thiocyanate analogs and that the exchange of thio- by selenocyanate leads to an increase in the magnetic intrachain interactions (Neumann *et al.*, 2019).



Unfortunately, the synthesis of compounds in which Co^{II} cations are linked by selenocyanate anions into chains in solution is always difficult to achieve or even impossible, because Co^{II} is not very chalcophilic and therefore, in most cases, compounds with terminally coordinated selenocyanate anions are obtained. To overcome this problem, we have developed an alternative approach for the synthesis of coordination networks based on thermal ligand removal of suitable precursor compounds that can be used for the synthesis of a wide range of materials including thio- and selenocyanates but also halide coordination compounds (Werner *et al.*, 2014; Boeckmann *et al.*, 2011; Näther & Jess, 2004). For thiocyanate compounds, the precursors usually consist of discrete complexes of the general formula $Co(NCS)_2(L)_4$ (L = monocoordinating coligand), in which the Co^{II} cations are octahedrally coordinated by two terminal N-bonded thiocyanate anions and four coligands. Upon heating, most of compounds of this type lose half of the ligands in the first mass loss and the

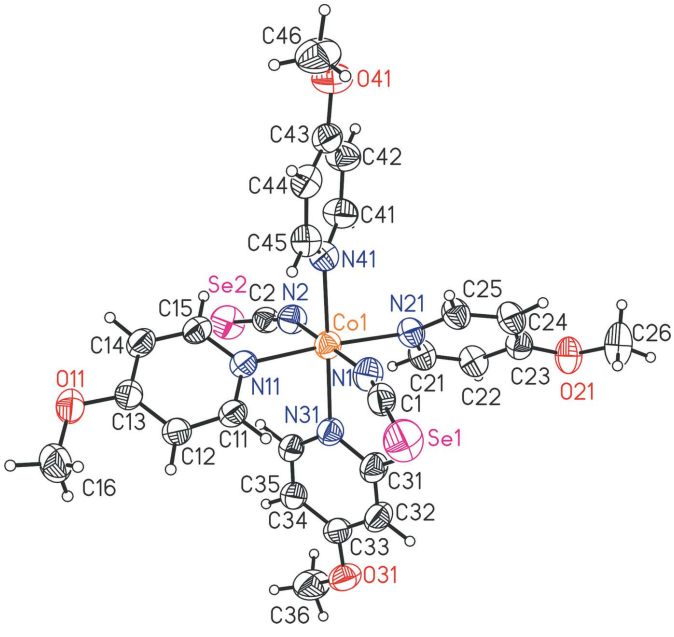


Figure 1
Crystal structure of the title compound with labeling and displacement ellipsoids drawn at the 50% probability level.

Table 1
Selected geometric parameters (Å, °).

Co1—N2	2.092 (2)	Co1—N21	2.170 (2)
Co1—N1	2.108 (2)	Co1—N41	2.174 (2)
Co1—N11	2.139 (2)	Co1—N31	2.203 (2)
N2—Co1—N1	178.93 (10)	N11—Co1—N41	91.26 (8)
N2—Co1—N11	90.65 (9)	N21—Co1—N41	92.61 (9)
N1—Co1—N11	90.00 (9)	N2—Co1—N31	88.71 (9)
N2—Co1—N21	90.08 (9)	N1—Co1—N31	90.47 (9)
N1—Co1—N21	89.20 (9)	N11—Co1—N31	88.32 (8)
N11—Co1—N21	176.06 (9)	N21—Co1—N31	87.83 (9)
N2—Co1—N41	90.07 (9)	N41—Co1—N31	178.70 (9)
N1—Co1—N41	90.76 (9)		

octahedral metal coordination is retained by the sulfur atoms that were not involved in the metal coordination in the precursor, which enforces the formation of compounds with bridging anionic ligands.

In the course of our systematic work we became interested in the corresponding $Co(NCSe)_2$ compounds with 4-methoxypyridine as coligand, because its thiocyanate analog $Co(NCS)_2$(4-methoxypyridine)$_2$ crystallizes in the desired chain structure and is well investigated. This compound shows a metamagnetic transition and single-chain relaxations and this was investigated on powders but also using single crystals (Rams *et al.*, 2020; Foltyn *et al.*, 2022). The reaction of $CoCl_2{\cdot}6H_2O$, KSeCN with 4-methoxypyridine in water, however, always led to the formation of a compound with the composition $Co(NCSe)_2$(4-methoxypyridine)$_4$ (see *Synthesis and crystallization*) for which the CN stretching vibration of the anionic ligand is observed at 2068 cm^{-1}, indicative for the presence of only terminally bonded selenocyanate anions (Fig. S1). Even if $CoCl_2{\cdot}6H_2O$ and KSeCN were used in excess, no other crystalline phase was obtained. To identify this phase unambiguously, single crystals were grown and characterized by single-crystal X-ray diffraction.

2. Structural commentary

Single-crystal structure determination proved that the title compound, $Co(NCSe)_2$(4-methoxypyridine)$_4$, consists of discrete complexes in which the Co cations are sixfold coordinated to four 4-methoxypyridine coligands and two terminal selenocyanate anions that coordinate *via* the N atom of the anionic ligand to the metal center (Fig. 1). The asymmetric unit consists of one Co^{II} cation, two selenocyanate anions and four 4-methoxypyridine ligands in general positions. From the bond lengths and angles, it is obvious that the octahedra are slightly distorted (Table 1). This is also obvious from the angle variance of 1.77 and the quadratic elongation of 1.00 calculated using the method of Robinson (Robinson *et al.*, 1971).

The title compound is isotypic to $M(NCS)_2$(4-methoxypyridine) (M = Co, Fe, Ni) already described in the literature (Mautner *et al.*, 2018; Jochim *et al.*, 2018). In this context, it is noted that $Ni(NCS)_2$(4-methoxypyridine) crystallizes in two polymorphic modifications, of which the form (orthorhombic, space group *Pccn*) that is not isotypic to the title compound and $M(NCS)_2$(4-methoxypyridine (M = Co, Fe) represents the

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C11—H11···O11^{i}	0.95	2.49	3.165 (3)	128
C15—H15···O31^{ii}	0.95	2.52	3.297 (3)	139
C16—H16B···Se1^{iii}	0.98	3.15	4.096 (3)	163
C22—H22···Se1^{iv}	0.95	3.12	3.817 (3)	132
C26—H26A···Se1^{v}	0.98	3.06	4.029 (5)	171
C36—H36B···Se2^{vi}	0.98	3.13	3.952 (4)	142
C41—H41···O21^{vii}	0.95	2.43	3.248 (4)	144
C45—H45···Se2^{viii}	0.95	3.08	3.932 (3)	151
C46—H46A···Se1^{ii}	0.98	3.15	3.885 (4)	133

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

thermodynamically stable phase at room temperature (Jochim *et al.*, 2018). However, from this experimental observation one cannot conclude that the title compound is metastable at room temperature and that a second form must exist. It is also noted that the thiocyanate analogs with manganese and cadmium crystallize in a third form (monoclinic, space group $C2/c$) and that the $Cd(NCS)_2$ compound also shows dimorphism and additionally crystallizes in a fourth form (tetragonal, space group $P4_1$), which shows the pronounced structural variability for such simple complexes (Jochim *et al.*, 2019). Finally, it is noted that we have not found any evidence that the title compound crystallizes in a further crystalline form.

3. Supramolecular features

In the crystal structure, the discrete complexes are arranged in an irregular manner (Fig. 2) There are a number of intermolecular C—H···O and C—H···Se contacts, but for most of them the C—H···X (X = O, Se) angle is far from linear and the H···X distances are too large for any significant interaction (Table 2). Some of C—H···Se contacts exhibit angles larger than 150°, which might point to some interaction (Fig. 2 and Table 2).

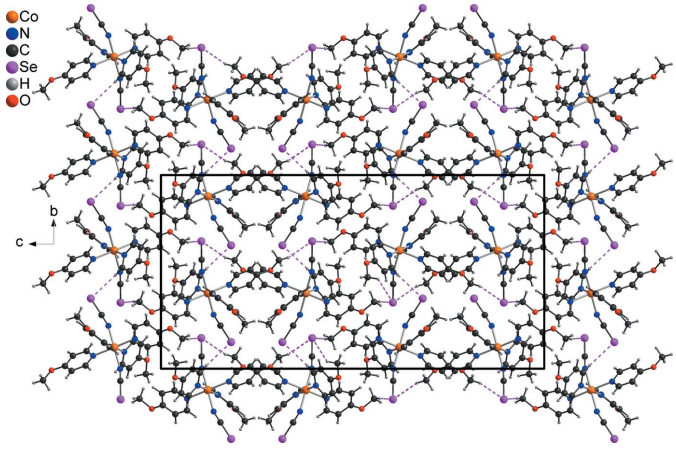


Figure 2
Crystal structure of the title compound viewed along the crystallographic a-axis direction. C—H···Se interactions are shown as pink dashed lines.

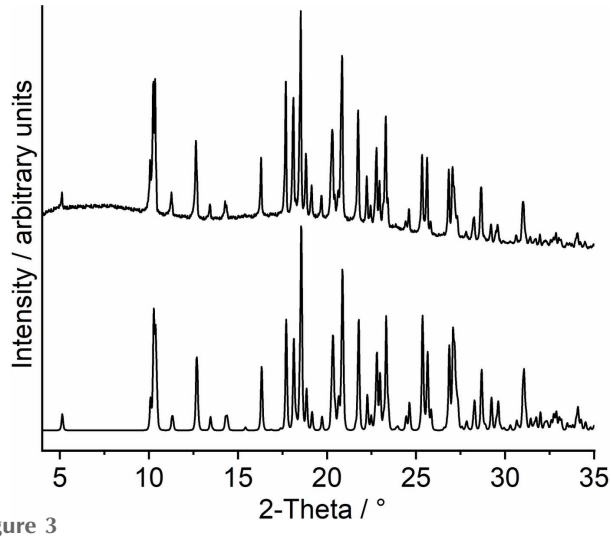


Figure 3
Experimental (top) and calculated PXRD pattern (bottom) of the title compound.

4. Thermal properties

Based on the single-crystal structural data, a powder pattern was calculated and compared with the experimental pattern, which shows that a pure crystalline phase was obtained (Fig. 3). To investigate if a crystalline ligand deficient phase with the composition $Co(NCS)_2(4\text{-methoxypyridine})_4$ can be obtained, measurements using differential thermal analysis and thermogravimetry with 8°C min^{-1} were performed. Upon heating, the TG curve shows two poorly resolved mass losses at about 160 and 250°C that are accompanied with endothermic events in the DTA curve (Fig. 4). The DTG curve indicates that the

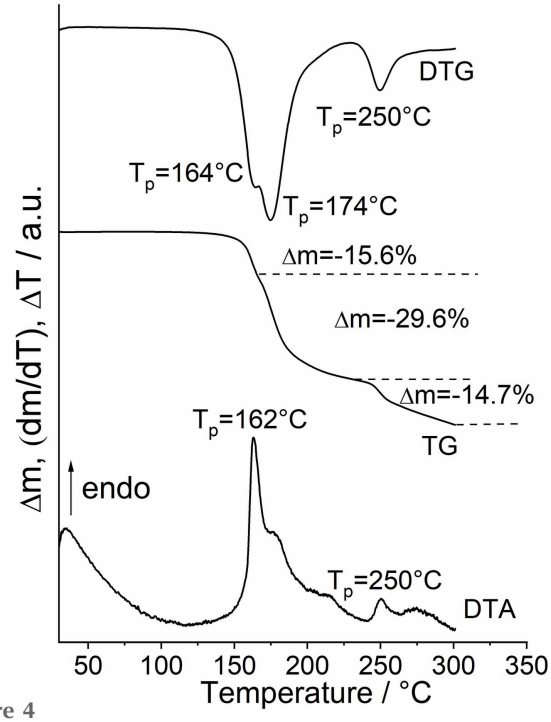


Figure 4
DTG, TG and DTA curves for the title compound measured at 8°C min^{-1} in a nitrogen atmosphere.

first event consists of two different thermal events that cannot be successfully resolved. Nevertheless, the experimental mass loss was calculated for all three events, which shows that the first mass loss is in reasonable agreement with that calculated for the removal of one 4-methoxypyridine ligand (Δm = −15.5%), whereas the second mass loss points to the removal of two additional 4-methoxypyridine ligands (Fig. 4). This would indicate that in the first step a compound with the composition $Co(NCSe)_2$(4-methoxypyridine)$_3$ is formed, which transforms into $Co(NCSe)_2$(4-methoxypyridine) upon further heating. Compounds with such a ratio between the metal salt and neutral coligands are known for thiocyanate coordination compounds, but are very rare for selenocyanates. One compound with the composition $Ni(NCSe)_2$[*N*,*N*′-bis(3-aminopropyl)methylamine]$_2$ is found in which each Ni cation is octahedrally coordinated by three N atoms of one (3-aminopropyl)methylamine ligand plus two bridging and two terminal selenocyanate anions (Vicente *et al.*, 1993). Two of the Ni cations are linked by pairs of μ-1,3-bridging anionic ligands into dinculear units. At first glance, the Ni:coligand ratio seems to be different but one (3-aminopropyl)methylamine ligand replaces three monocoordinating ligands. For a ratio of 1:1 between $M(NCS)_2$ and coligand, no examples can be found with selenocyanate anions but a few examples with thiocyanate are reported in the literature, including $Ni(NCS)_2$(4-aminopyridine), in which $Ni(NCS)_2$ double chains are observed (Neumann *et al.*, 2018).

To increase the resolution, measurements at different heating rates were performed, but the TG curves look similar and are still poorly resolved (Fig. S2). However, to investigate if different crystalline phases can be prepared, the residues obtained at different temperatures were isolated and investigated by PXRD, which proved that they are amorphous, and in Fig. S3 one of these patterns is shown as a representative. We also tried to anneal samples of the title compound at constant temperatures but always obtained amorphous intermediates. Therefore, no more efforts were made.

5. Database survey

In the CCDC database, no selenocyanate compounds with 4-methoxypyridine are reported (CSD version 5.42, last update November 2021; Groom *et al.*, 2016), but some compounds with thiocyanate as the anionic ligand are found. They include compounds with the composition $M(NCS)_2$(4-methoxypyridine)$_4$ with *M* = Mn (Refcode COBVEX; Jochim *et al.*, 2019), Fe (Refcode FISCIW; Jochim *et al.*, 2018), Co (Refcode KIJPUR; Mautner *et al.*, 2018), Ni (Refcodes FISCAO and FISCES; Jochim *et al.*, 2019), Cd (Refcode COBTUL and COBTUL01; Jochim *et al.*, 2019) and Ru (Refcode NAGPOD; Cadranel *et al.*, 2016), which form discrete complexes with octahedral coordination. All of these compounds crystallize in four different structure types. There are additional discrete octahedral complexes with the composition $Cd(NCS)_2$(4-methoxypyridine)$_2$·4-methoxypyridine (Refcode COBVAT; Jochim *et al.*, 2019) and $Ni(NCS)_2$(4-methoxypyridine)$_2$·acetonitrile (Refcode FISCOC; Jochim *et al.*, 2018) that form solvates and one acetonitrile complex with the composition $Ni(NCS)_2$(4-methoxypyridine)$_2(CH_3CN)_2$ (Refcode FISCES; Jochim *et al.*, 2018).

With thiocyanate, compounds are reported with the composition $M(NCS)_2$(4-methoxypyridine)$_2$ with *M* = Cu (Refcode ABOXAT; Handy *et al.*, 2017), Co (KIJQAY, KIJPOL and KIJPOL01; Mautner *et al.*, 2018 and Rams *et al.*, 2020), Ni (FISBUH; Jochim *et al.*, 2018), Cd (COBTUL and COBVIB; Jochim *et al.*, 2019). The Cu compound forms discrete complexes with a square-planar coordination, while the Co compounds consist of isomers forming discrete tetrahedral complexes as well as a chain compound with an octahedral coordination, which is also the case for the Co and Cd compounds.

There are also discrete complexes with selenocyanate anions and pyridine derivatives as coligands reported in the literature that are comparable to the title compound. These include, for example, $Fe(NCSe)_2$[4-2(phenylvinyl)pyridine-N]$_4$ (Refcodes XUKNUN, XUKNUN01, XUKPEZ and XUKPEZ01; Boillot *et al.*, 2009) and $Co(NCSe)_2$ [Refcodes ITISOU (Boeckmann & Näther, 2011) and TIXDOW, TIXDOW01 and TIXFAK (Neumann *et al.*, 2019)].

6. Synthesis and crystallization

$CoCl_2·6H_2O$ and KSeCN were purchased from Aldrich and 4-methoxypyridine was purchased from Alfa Aesar.

Synthesis:

Larger amounts of a microcrystalline powder were obtained by the reaction of 0.15 mmol (35.7 mg) of $CoCl_2·6H_2O$ with 0.30 mmol (43.3 mg) of KSeCN and 0.60 mmol (60.8 µL) of 4-methoxypyridine in 1 ml of demineralized water. The mixture was stirred for 2 d at room temperature, the light-pink-colored precipitate was filtered off and washed with a very small amount of water. Single crystals were obtained by slow evaporation of the solvent from the filtrate. It is noted that the same compound is obtained if $CoCl_2·6H_2O$ and 4-methoxypyridine are used in a 1:1 ratio.

Experimental details:

The XRPD measurements were performed with a Stoe Transmission Powder Diffraction System (STADI P) equipped with a MYTHEN 1K detector and a Johansson-type Ge(111) monochromator using Cu $K\alpha_1$ radiation (λ = 1.540598 Å). The IR spectra were measured using an ATI Mattson Genesis Series FTIR Spectrometer, control software: *WINFIRST*, from ATI Mattson. Thermogravimetry and differential thermoanalysis (TG–DTA) measurements were performed in a dynamic nitrogen atmosphere in Al_2O_3 crucibles using a STA-PT 1000 thermobalance from Linseis. The instrument was calibrated using standard reference materials.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. Hydrogen atoms were positioned with idealized geometry (C—H = 0.95–0.98 Å, methyl H atoms

Table 3
Experimental details.

Crystal data	
Chemical formula	$[Co(NCSe)_2(C_6H_7NO)_4]$
M_r	705.39
Crystal system, space group	Orthorhombic, *Pbca*
Temperature (K)	200
a, *b*, *c* (Å)	10.0531 (2), 17.3479 (4), 34.3141 (5)
V (Å^3)	5984.4 (2)
Z	8
Radiation type	Mo *Kα*
μ (mm^{-1})	3.05
Crystal size (mm)	0.23 × 0.19 × 0.17
Data collection	
Diffractometer	Stoe *IPDS2*
Absorption correction	Numerical (*X-RED* and *X-SHAPE*; Stoe, 2008)
T_{min}, T_{max}	0.457, 0.738
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	56525, 5862, 5130
R_{int}	0.035
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.038, 0.087, 1.07
No. of reflections	5862
No. of parameters	356
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.34, −0.48

Computer programs: *X-AREA* (Stoe, 2008), *SHELXT2014/5* (Sheldrick, 2015*a*), *SHELXL2016/6* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg & Putz, 1999) and *publCIF* (Westrip, 2010).

allowed to rotate but not to tip) and were refined with U_{iso}(H) = 1.2U_{eq}(C) (1.5 for methyl H atoms) using a riding model.

Acknowledgements

This work was supported by the State of Schleswig-Holstein.

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supporting information

Acta Cryst. (2023). E**79**, 216-220 [https://doi.org/10.1107/S2056989023001391]

Synthesis, crystal structure and properties of bis(isoselenocyanato-κ*N*)tetrakis-(4-methoxypyridine-κ*N*)cobalt(II)

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Computing details

Data collection: *X-AREA* (Stoe, 2008); cell refinement: *X-AREA* (Stoe, 2008); data reduction: *X-AREA* (Stoe, 2008); program(s) used to solve structure: *SHELXT2014/5* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2016/6* (Sheldrick, 2015b); molecular graphics: *DIAMOND* (Brandenburg & Putz, 1999); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Bis(isoselenocyanato-κ*N*)tetrakis(4-methoxypyridine-κ*N*)cobalt(II)

Crystal data

$[Co(NCSe)_2(C_6H_7NO)_4]$
M_r = 705.39
Orthorhombic, *Pbca*
a = 10.0531 (2) Å
b = 17.3479 (4) Å
c = 34.3141 (5) Å
V = 5984.4 (2) Å^3
Z = 8
F(000) = 2824
D_x = 1.566 Mg m^{-3}
Mo *Kα* radiation, λ = 0.71073 Å
Cell parameters from 56525 reflections
θ = 1.2–26.0°
μ = 3.05 mm^{-1}
T = 200 K
Block, light pink
0.23 × 0.19 × 0.17 mm

Data collection

Stoe IPDS-2 diffractometer
ω scans
Absorption correction: numerical (X-Red and X-Shape; Stoe, 2008)
T_{min} = 0.457, T_{max} = 0.738
56525 measured reflections
5862 independent reflections
5130 reflections with $I > 2\sigma(I)$
R_{int} = 0.035
θ_{max} = 26.0°, θ_{min} = 1.2°
h = −12→9
k = −21→21
l = −42→42

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.087
S = 1.07
5862 reflections
356 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0382P)^2 + 4.2748P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.003
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.47 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Co1	0.42296 (4)	0.38984 (2)	0.62207 (2)	0.04280 (10)
N1	0.4898 (3)	0.50081 (14)	0.60651 (7)	0.0509 (5)
C1	0.5320 (3)	0.56297 (17)	0.60594 (8)	0.0479 (6)
Se1	0.59634 (4)	0.65844 (2)	0.60535 (2)	0.07361 (13)
N2	0.3601 (2)	0.27886 (13)	0.63726 (7)	0.0504 (5)
C2	0.3463 (3)	0.22263 (16)	0.65509 (8)	0.0453 (6)
Se2	0.32769 (4)	0.13723 (2)	0.68306 (2)	0.06769 (12)
N11	0.3567 (2)	0.43341 (13)	0.67705 (6)	0.0426 (5)
C11	0.4297 (3)	0.48409 (16)	0.69698 (8)	0.0449 (6)
H11	0.508929	0.502719	0.685193	0.054*
C12	0.3978 (3)	0.51110 (16)	0.73342 (7)	0.0435 (6)
H12	0.454554	0.546307	0.746578	0.052*
C13	0.2809 (3)	0.48581 (15)	0.75052 (8)	0.0443 (6)
C14	0.2031 (3)	0.43319 (16)	0.72997 (8)	0.0482 (6)
H14	0.122509	0.414453	0.740865	0.058*
C15	0.2436 (3)	0.40891 (15)	0.69422 (8)	0.0449 (6)
H15	0.189538	0.372893	0.680651	0.054*
O11	0.2361 (2)	0.50833 (14)	0.78569 (6)	0.0613 (5)
C16	0.3177 (4)	0.5600 (2)	0.80767 (10)	0.0743 (10)
H16A	0.402605	0.534966	0.813740	0.111*
H16B	0.272280	0.573788	0.831961	0.111*
H16C	0.334262	0.606763	0.792371	0.111*
N21	0.5040 (2)	0.34562 (13)	0.56789 (6)	0.0469 (5)
C21	0.5856 (3)	0.28430 (16)	0.56790 (8)	0.0496 (6)
H21	0.587114	0.252310	0.590368	0.059*
C22	0.6666 (3)	0.26539 (16)	0.53735 (8)	0.0512 (7)
H22	0.722378	0.221281	0.538708	0.061*
C23	0.6661 (3)	0.31148 (15)	0.50441 (8)	0.0475 (6)
C24	0.5771 (3)	0.37243 (16)	0.50266 (8)	0.0523 (7)
H24	0.569119	0.403015	0.479818	0.063*
C25	0.5007 (3)	0.38721 (17)	0.53511 (8)	0.0510 (7)
H25	0.441604	0.429897	0.534145	0.061*
O21	0.7538 (2)	0.29286 (12)	0.47615 (6)	0.0593 (5)
C26	0.7672 (4)	0.3449 (2)	0.44407 (10)	0.0761 (11)
H26A	0.683599	0.346536	0.429403	0.114*
H26B	0.839033	0.327220	0.426951	0.114*
H26C	0.788117	0.396546	0.453862	0.114*
N31	0.6165 (2)	0.36451 (13)	0.64936 (6)	0.0441 (5)
C31	0.7328 (3)	0.38797 (17)	0.63423 (8)	0.0513 (7)

H31	0.730644	0.422024	0.612555	0.062*
C32	0.8543 (3)	0.36555 (18)	0.64827 (9)	0.0552 (7)
H32	0.933751	0.384252	0.636632	0.066*
C33	0.8602 (3)	0.31539 (17)	0.67957 (8)	0.0468 (6)
C34	0.7418 (3)	0.29132 (16)	0.69587 (8)	0.0478 (6)
H34	0.741410	0.257422	0.717608	0.057*
C35	0.6246 (3)	0.31725 (17)	0.68008 (7)	0.0463 (6)
H35	0.543881	0.300535	0.691747	0.056*
O31	0.9822 (2)	0.29425 (13)	0.69180 (6)	0.0613 (5)
C36	0.9907 (4)	0.2312 (2)	0.71856 (11)	0.0772 (10)
H36A	0.949864	0.245955	0.743396	0.116*
H36B	1.084362	0.217962	0.722851	0.116*
H36C	0.943834	0.186517	0.707773	0.116*
N41	0.2300 (2)	0.41270 (13)	0.59591 (6)	0.0471 (5)
C41	0.1720 (3)	0.36068 (17)	0.57240 (9)	0.0562 (7)
H41	0.214155	0.312096	0.569187	0.067*
C42	0.0557 (3)	0.37370 (19)	0.55288 (9)	0.0592 (8)
H42	0.019107	0.335190	0.536376	0.071*
C43	−0.0080 (3)	0.44397 (18)	0.55750 (8)	0.0512 (6)
C44	0.0467 (3)	0.49680 (16)	0.58295 (8)	0.0505 (7)
H44	0.003580	0.544520	0.587894	0.061*
C45	0.1652 (3)	0.47896 (15)	0.60105 (8)	0.0476 (6)
H45	0.202896	0.516039	0.618178	0.057*
O41	−0.1208 (2)	0.45430 (15)	0.53667 (7)	0.0696 (6)
C46	−0.1853 (4)	0.5276 (2)	0.53937 (13)	0.0798 (11)
H46A	−0.212437	0.536910	0.566395	0.120*
H46B	−0.263923	0.528030	0.522492	0.120*
H46C	−0.123661	0.568224	0.531068	0.120*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.04374 (19)	0.04212 (19)	0.04252 (19)	−0.00171 (15)	0.00192 (15)	0.00372 (14)
N1	0.0553 (14)	0.0453 (13)	0.0522 (13)	−0.0025 (11)	0.0056 (11)	0.0050 (10)
C1	0.0508 (16)	0.0524 (16)	0.0405 (13)	0.0026 (13)	0.0043 (12)	0.0047 (11)
Se1	0.0947 (3)	0.05033 (18)	0.0758 (2)	−0.02052 (18)	0.00388 (19)	0.00265 (15)
N2	0.0518 (14)	0.0460 (13)	0.0532 (13)	−0.0049 (11)	−0.0007 (11)	0.0044 (11)
C2	0.0431 (14)	0.0463 (15)	0.0465 (14)	−0.0031 (12)	−0.0012 (11)	−0.0067 (12)
Se2	0.0820 (3)	0.04693 (18)	0.0741 (2)	−0.00859 (16)	−0.00418 (18)	0.01474 (15)
N11	0.0373 (11)	0.0470 (12)	0.0435 (11)	−0.0019 (9)	0.0011 (9)	0.0020 (9)
C11	0.0371 (13)	0.0513 (15)	0.0463 (14)	−0.0056 (11)	0.0006 (11)	0.0047 (11)
C12	0.0393 (14)	0.0477 (14)	0.0436 (13)	−0.0030 (11)	−0.0023 (11)	0.0031 (11)
C13	0.0431 (14)	0.0473 (14)	0.0426 (13)	0.0031 (12)	0.0030 (11)	0.0028 (11)
C14	0.0386 (14)	0.0539 (16)	0.0523 (15)	−0.0053 (12)	0.0053 (12)	0.0034 (12)
C15	0.0377 (13)	0.0459 (14)	0.0511 (14)	−0.0042 (11)	0.0014 (11)	0.0028 (11)
O11	0.0571 (12)	0.0760 (14)	0.0509 (11)	−0.0092 (11)	0.0127 (10)	−0.0123 (10)
C16	0.082 (2)	0.082 (2)	0.0585 (19)	−0.018 (2)	0.0122 (17)	−0.0227 (17)
N21	0.0525 (14)	0.0458 (12)	0.0424 (11)	0.0030 (10)	0.0003 (10)	0.0025 (9)

C21	0.0608 (17)	0.0426 (14)	0.0452 (14)	0.0043 (13)	0.0002 (12)	0.0034 (11)
C22	0.0617 (18)	0.0419 (14)	0.0499 (15)	0.0077 (13)	−0.0003 (13)	−0.0001 (12)
C23	0.0534 (16)	0.0433 (14)	0.0457 (14)	−0.0035 (12)	0.0041 (12)	−0.0052 (11)
C24	0.0649 (18)	0.0483 (15)	0.0436 (14)	0.0069 (13)	−0.0003 (13)	0.0044 (12)
C25	0.0568 (17)	0.0528 (16)	0.0434 (14)	0.0098 (13)	−0.0011 (13)	0.0033 (12)
O21	0.0743 (14)	0.0504 (11)	0.0532 (11)	0.0053 (10)	0.0172 (10)	−0.0017 (9)
C26	0.101 (3)	0.0597 (19)	0.067 (2)	0.0058 (19)	0.035 (2)	0.0068 (16)
N31	0.0420 (12)	0.0459 (12)	0.0445 (11)	−0.0011 (10)	0.0022 (9)	0.0036 (9)
C31	0.0481 (16)	0.0540 (16)	0.0520 (15)	−0.0062 (13)	0.0044 (12)	0.0114 (13)
C32	0.0437 (15)	0.0617 (18)	0.0601 (17)	−0.0075 (14)	0.0074 (13)	0.0104 (14)
C33	0.0404 (14)	0.0499 (15)	0.0501 (14)	−0.0031 (12)	−0.0030 (12)	−0.0017 (12)
C34	0.0472 (15)	0.0512 (15)	0.0450 (14)	−0.0061 (12)	−0.0002 (12)	0.0063 (12)
C35	0.0415 (14)	0.0542 (15)	0.0432 (13)	−0.0051 (12)	0.0035 (11)	0.0063 (12)
O31	0.0428 (11)	0.0712 (14)	0.0700 (13)	−0.0044 (10)	−0.0064 (10)	0.0116 (11)
C36	0.058 (2)	0.090 (3)	0.084 (2)	0.0044 (19)	−0.0175 (18)	0.027 (2)
N41	0.0496 (13)	0.0450 (12)	0.0466 (12)	0.0013 (10)	−0.0008 (10)	0.0004 (9)
C41	0.0558 (18)	0.0505 (16)	0.0623 (17)	0.0076 (14)	−0.0092 (14)	−0.0121 (13)
C42	0.0569 (18)	0.0586 (18)	0.0620 (18)	0.0030 (14)	−0.0083 (14)	−0.0128 (14)
C43	0.0437 (15)	0.0586 (17)	0.0513 (15)	0.0013 (13)	0.0005 (12)	0.0066 (13)
C44	0.0502 (16)	0.0450 (14)	0.0563 (16)	0.0032 (12)	0.0064 (13)	0.0053 (12)
C45	0.0524 (16)	0.0408 (13)	0.0494 (15)	−0.0002 (12)	0.0019 (12)	0.0016 (11)
O41	0.0531 (13)	0.0749 (15)	0.0807 (15)	0.0082 (12)	−0.0151 (11)	0.0034 (12)
C46	0.061 (2)	0.076 (2)	0.102 (3)	0.0171 (18)	−0.013 (2)	0.017 (2)

Geometric parameters (Å, º)

Co1—N2	2.092 (2)	C25—H25	0.9500
Co1—N1	2.108 (2)	O21—C26	1.430 (4)
Co1—N11	2.139 (2)	C26—H26A	0.9800
Co1—N21	2.170 (2)	C26—H26B	0.9800
Co1—N41	2.174 (2)	C26—H26C	0.9800
Co1—N31	2.203 (2)	N31—C35	1.338 (3)
N1—C1	1.159 (4)	N31—C31	1.342 (4)
C1—Se1	1.778 (3)	C31—C32	1.370 (4)
N2—C2	1.160 (3)	C31—H31	0.9500
C2—Se2	1.775 (3)	C32—C33	1.384 (4)
N11—C11	1.334 (3)	C32—H32	0.9500
N11—C15	1.349 (3)	C33—O31	1.347 (3)
C11—C12	1.373 (4)	C33—C34	1.379 (4)
C11—H11	0.9500	C34—C35	1.373 (4)
C12—C13	1.384 (4)	C34—H34	0.9500
C12—H12	0.9500	C35—H35	0.9500
C13—O11	1.346 (3)	O31—C36	1.431 (4)
C13—C14	1.393 (4)	C36—H36A	0.9800
C14—C15	1.359 (4)	C36—H36B	0.9800
C14—H14	0.9500	C36—H36C	0.9800
C15—H15	0.9500	N41—C45	1.333 (3)
O11—C16	1.431 (4)	N41—C41	1.344 (4)

C16—H16A	0.9800	C41—C42	1.366 (4)
C16—H16B	0.9800	C41—H41	0.9500
C16—H16C	0.9800	C42—C43	1.386 (4)
N21—C25	1.337 (3)	C42—H42	0.9500
N21—C21	1.343 (3)	C43—O41	1.353 (3)
C21—C22	1.367 (4)	C43—C44	1.380 (4)
C21—H21	0.9500	C44—C45	1.379 (4)
C22—C23	1.384 (4)	C44—H44	0.9500
C22—H22	0.9500	C45—H45	0.9500
C23—O21	1.350 (3)	O41—C46	1.431 (4)
C23—C24	1.386 (4)	C46—H46A	0.9800
C24—C25	1.377 (4)	C46—H46B	0.9800
C24—H24	0.9500	C46—H46C	0.9800

N2—Co1—N1	178.93 (10)	N21—C25—H25	117.8
N2—Co1—N11	90.65 (9)	C24—C25—H25	117.8
N1—Co1—N11	90.00 (9)	C23—O21—C26	117.6 (2)
N2—Co1—N21	90.08 (9)	O21—C26—H26A	109.5
N1—Co1—N21	89.20 (9)	O21—C26—H26B	109.5
N11—Co1—N21	176.06 (9)	H26A—C26—H26B	109.5
N2—Co1—N41	90.07 (9)	O21—C26—H26C	109.5
N1—Co1—N41	90.76 (9)	H26A—C26—H26C	109.5
N11—Co1—N41	91.26 (8)	H26B—C26—H26C	109.5
N21—Co1—N41	92.61 (9)	C35—N31—C31	115.9 (2)
N2—Co1—N31	88.71 (9)	C35—N31—Co1	120.72 (18)
N1—Co1—N31	90.47 (9)	C31—N31—Co1	122.96 (18)
N11—Co1—N31	88.32 (8)	N31—C31—C32	123.7 (3)
N21—Co1—N31	87.83 (9)	N31—C31—H31	118.2
N41—Co1—N31	178.70 (9)	C32—C31—H31	118.2
C1—N1—Co1	166.1 (2)	C31—C32—C33	119.3 (3)
N1—C1—Se1	179.7 (3)	C31—C32—H32	120.3
C2—N2—Co1	160.3 (2)	C33—C32—H32	120.3
N2—C2—Se2	178.8 (3)	O31—C33—C34	125.2 (3)
C11—N11—C15	116.6 (2)	O31—C33—C32	116.9 (3)
C11—N11—Co1	120.90 (17)	C34—C33—C32	117.9 (3)
C15—N11—Co1	122.44 (18)	C35—C34—C33	118.8 (2)
N11—C11—C12	124.3 (2)	C35—C34—H34	120.6
N11—C11—H11	117.9	C33—C34—H34	120.6
C12—C11—H11	117.9	N31—C35—C34	124.3 (3)
C11—C12—C13	118.4 (2)	N31—C35—H35	117.8
C11—C12—H12	120.8	C34—C35—H35	117.8
C13—C12—H12	120.8	C33—O31—C36	117.6 (2)
O11—C13—C12	124.9 (3)	O31—C36—H36A	109.5
O11—C13—C14	117.1 (2)	O31—C36—H36B	109.5
C12—C13—C14	118.0 (2)	H36A—C36—H36B	109.5
C15—C14—C13	119.4 (2)	O31—C36—H36C	109.5
C15—C14—H14	120.3	H36A—C36—H36C	109.5
C13—C14—H14	120.3	H36B—C36—H36C	109.5

N11—C15—C14	123.3 (3)	C45—N41—C41	116.5 (2)
N11—C15—H15	118.4	C45—N41—Co1	122.59 (19)
C14—C15—H15	118.4	C41—N41—Co1	120.87 (19)
C13—O11—C16	117.5 (2)	N41—C41—C42	123.7 (3)
O11—C16—H16A	109.5	N41—C41—H41	118.1
O11—C16—H16B	109.5	C42—C41—H41	118.1
H16A—C16—H16B	109.5	C41—C42—C43	119.0 (3)
O11—C16—H16C	109.5	C41—C42—H42	120.5
H16A—C16—H16C	109.5	C43—C42—H42	120.5
H16B—C16—H16C	109.5	O41—C43—C44	125.5 (3)
C25—N21—C21	116.3 (2)	O41—C43—C42	116.3 (3)
C25—N21—Co1	121.38 (19)	C44—C43—C42	118.2 (3)
C21—N21—Co1	120.60 (18)	C45—C44—C43	118.7 (3)
N21—C21—C22	123.6 (3)	C45—C44—H44	120.6
N21—C21—H21	118.2	C43—C44—H44	120.6
C22—C21—H21	118.2	N41—C45—C44	123.8 (3)
C21—C22—C23	119.0 (3)	N41—C45—H45	118.1
C21—C22—H22	120.5	C44—C45—H45	118.1
C23—C22—H22	120.5	C43—O41—C46	117.6 (3)
O21—C23—C22	116.5 (3)	O41—C46—H46A	109.5
O21—C23—C24	125.0 (3)	O41—C46—H46B	109.5
C22—C23—C24	118.6 (3)	H46A—C46—H46B	109.5
C25—C24—C23	117.8 (3)	O41—C46—H46C	109.5
C25—C24—H24	121.1	H46A—C46—H46C	109.5
C23—C24—H24	121.1	H46B—C46—H46C	109.5
N21—C25—C24	124.5 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C11—H11···O11^{i}	0.95	2.49	3.165 (3)	128
C15—H15···O31^{ii}	0.95	2.52	3.297 (3)	139
C16—H16*B*···Se1^{iii}	0.98	3.15	4.096 (3)	163
C22—H22···Se1^{iv}	0.95	3.12	3.817 (3)	132
C26—H26*A*···Se1^{v}	0.98	3.06	4.029 (5)	171
C36—H36*B*···Se2^{vi}	0.98	3.13	3.952 (4)	142
C41—H41···O21^{vii}	0.95	2.43	3.248 (4)	144
C45—H45···Se2^{viii}	0.95	3.08	3.932 (3)	151
C46—H46*A*···Se1^{ii}	0.98	3.15	3.885 (4)	133

Symmetry codes: (i) *x*+1/2, *y*, −*z*+3/2; (ii) *x*−1, *y*, *z*; (iii) *x*−1/2, *y*, −*z*+3/2; (iv) −*x*+3/2, *y*−1/2, *z*; (v) −*x*+1, −*y*+1, −*z*+1; (vi) *x*+1, *y*, *z*; (vii) *x*−1/2, −*y*+1/2, −*z*+1; (viii) −*x*+1/2, *y*+1/2, *z*.