Acta Crystallographica Section C
**Crystal Structure Communications**
ISSN 0108-2701

# *catena*-Poly[[[*N*,*N*′-bis(salicylidene)-propane-1,3-diaminato]cobalt(III)]-*μ*-azido] and *catena*-poly[[[*N*,*N*′-bis-(salicylidene)propane-1,3-diaminato]-cobalt(III)]-*μ*-thiocyanato]

**Zhong-Lu You**

Department of Chemistry and Chemical Engineering, Liaoning Normal University, Dalian 116029, People's Republic of China
Correspondence e-mail: youzhonglu@yahoo.com.cn

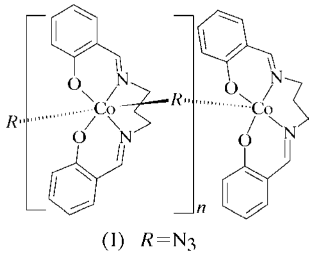
Received 18 April 2005
Accepted 20 April 2005
Online 13 May 2005

The two title complexes, *catena*-poly[[{2,2′-[1,3-propanediylbis(nitrilomethylidyne)]diphenolato}cobalt(III)]-*μ*-azido], [Co($C_{17}H_{16}N_2O_2$)($N_3$)]$_n$, (I), and *catena*-poly[[{2,2′-[1,3-propanediylbis(nitrilomethylidyne)]diphenolato}cobalt(III)]-*μ*-thiocyanato], [Co($C_{17}H_{16}N_2O_2$)(NCS)]$_n$, (II), are isomorphous polynuclear cobalt(III) compounds. In both structures, the Co$^{III}$ atom is six-coordinated in an octahedral configuration by two N atoms and two O atoms of one Schiff base, and two terminal N or S atoms from two bridging ligands. The [*N*,*N*′-bis(salicylidene)propane-1,3-diaminato]cobalt(III) moieties are linked by the bridging ligands, *viz*. azide in (I) and thiocyanate in (II), giving zigzag polymeric chains with backbones of the type [–Co—N—N—N—Co]$_n$ in (I) or [–Co—N—C—S—Co]$_n$ in (II) running along the *c* axis.

## Comment

Investigations of the magnetic properties of molecule-based materials containing a polymetallic assembly have become a fascinating subject in the field of condensed matter physics and materials chemistry (Dalai *et al.*, 2002; Bhaduri *et al.*, 2003). Much attention has been focused on coordination complexes with novel magnetic properties, which may have potentially useful applications in materials science (Ray *et al.*, 2003). The prime strategy for designing these molecular materials is to use a suitable bridging ligand that determines the nature of the magnetic interactions (Koner *et al.*, 2003).

Our work is aimed at obtaining multidimensional polymetallic complexes. Based on the above considerations, we designed and synthesized a flexible tetradentate ligand, namely *N*,*N*′-bis(salicylidene)-1,3-propanediamine (BSPD). The reason we did not use a rigid ligand is that the flexible BSPD ligand can adopt different coordination modes according to the geometric need of the transition metal ion and the coordination environment. The second ligand, *viz*. azide or thiocyanate, is a well known bridging group. They readily bridge different metal ions through their terminal donor atoms, forming polynuclear complexes. Cobalt(III) is a good candidate from octahedral coordination geometry. We report here a pair of interesting one-dimensional infinite chains formed by the reaction of the BSPD ligand and the azide or thiocyanate ligand with cobalt(III) acetate.



(I) *R*=$N_3$
(II) *R*=NCS

The two title complexes, (I) and (II), are isomorphous polynuclear cobalt(III) compounds (Figs. 1 and 2). In both structures, the smallest repeat unit contains two BSPD–Co$^{III}$ cations and two bridging ligands, *viz*. azide for (I) and thiocyanate for (II). The Co$^{III}$ atom is in an octahedral coordination environment and is six-coordinated by two N atoms and two O atoms of one Schiff base ligand defining the basal plane, and by two different but symmetry-related terminal N atoms [for (I)] or two terminal N and S atoms [for (II)] occupying the axial positions.

The angles subtended at atom Co1 in (I) are comparable with the corresponding values observed in (II) (Table 1). The bond angles formed by the two apical donor atoms and the Co$^{III}$ atom deviate from 180° by 15.53 (13) and 11.46 (16)° for (I) and (II), respectively, which is due to the strain created by

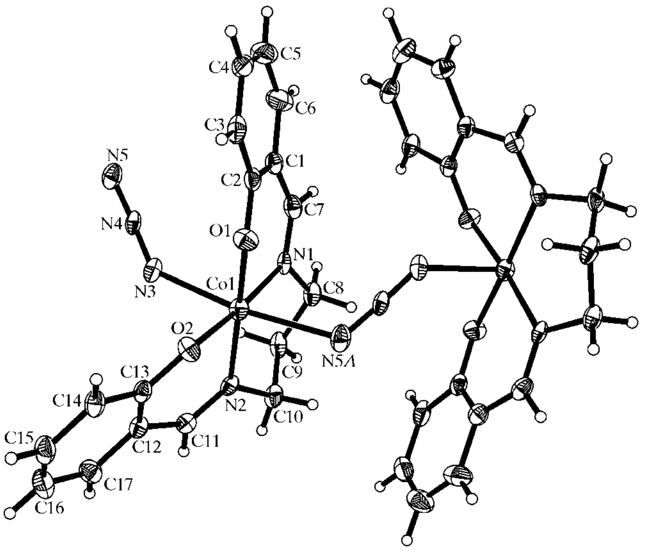


**Figure 1**
The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Unlabelled atoms or those labelled with the suffix *A* are at the symmetry position (1 − *x*, −*y*, $\frac{1}{2}$ + *z*).

DOI: 10.1107/S0108270105012497 © 2005 International Union of Crystallography

the two *cis*-bridging ligands related to the apical axis of the octahedron in the two complexes. The mean Co—N(imine) and mean Co—O(phenolate) bond lengths in (I) are also comparable with the corresponding values in (II). However, the bond lengths between atom Co1 and the apical donor atoms are different in the two compounds. The fact that the Co1—N3 bond length [2.352 (4) Å] in (I) is longer than that in (II) [2.262 (5) Å], while the Co1—N5$^{i}$ bond length in (I) [2.314 (4) Å] is much shorter than the Co1—S1$^{ii}$ bond length [2.781 (5) Å] in (II) [symmetry codes: (i) $1 - x$, $-y$, $\frac{1}{2} + z$; (ii) $1 - x$, $-y$, $\frac{1}{2} + z$] indicates that the Co—S bond is not very strong.

The conformations of the six-membered chelate rings containing the Co$^{III}$ atom, the azomethine N atoms and three C atoms (C8, C9 and C10) in both (I) and (II) are chair-shaped. The distances of the two *para*-positioned atoms, Co1 and C9, from the mean plane of the other four atoms are 0.473 (3) and −0.722 (6) Å, respectively, for (I), and 0.374 (3) and −0.753 (6) Å, respectively, for (II). In (I), the $CoN_2O_2$ basal plane forms dihedral angles of 20.5 (2) and 23.5 (2)° with the two phenolate ring systems, which are inclined at 43.8 (2)° to each other, while in (II), the $CoN_2O_2$ basal plane forms dihedral angles of 22.1 (2) and 14.8 (2)° with the two phenolate ring systems, which are inclined at 36.8 (2)° to each other.

In both complexes, the average C7═N1 and C11═N2 bond lengths [1.273 (6) Å in (I) and 1.286 (6) Å in (II)] conform to the normal value for double bonds, while the average C8—N1 and C10—N2 bond lengths [1.474 (5) Å in (I) and 1.466 (6) Å in (II)] conform to the normal value for single bonds (You & Zhu, 2004).

In the title crystal structures, the [*N*,*N*′-bis(salicylidene)-propane-1,3-diaminato]cobalt(III) moieties are linked by the bridging ligands, *viz*. azide for (I) and thiocyanate for (II), giving zigzag polymeric chains with backbones of the type $[-Co-N-N-N-Co]_n$ in (I) or $[-Co-N-C-S-Co]_n$ in (II) running along the *c* axis. There are no short intermolecular contacts.

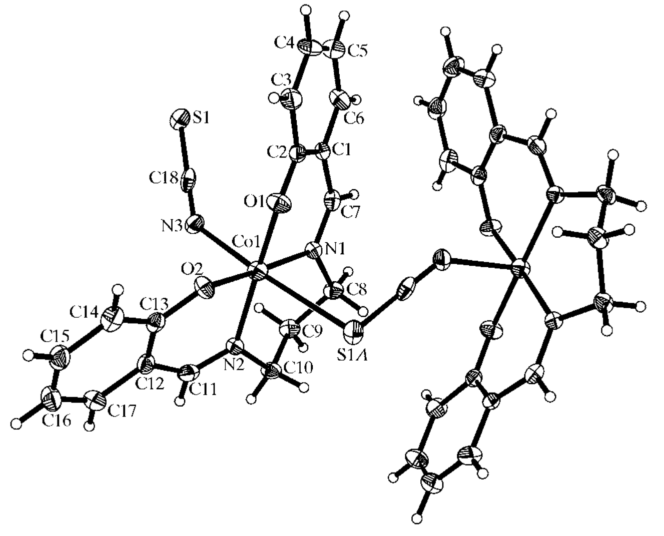


**Figure 2**
The structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Unlabelled atoms or those labelled with the suffix *A* are at the symmetry position ($1 - x$, $-y$, $\frac{1}{2} + z$).

## Experimental

For the preparation of complex (I), salicylaldehyde (0.1 mmol, 12.2 mg) and 1,3-diaminopropane (0.1 mmol, 7.4 mg) were dissolved in MeOH (10 ml). The mixture was stirred at room temperature for 10 min to give a yellow solution, to which was added an aqueous solution (2 ml) of $NaN_3$ (0.1 mmol, 6.5 mg) and an MeOH solution (3 ml) of $Co(ClO_4)_3 \cdot 7H_2O$ (0.1 mmol, 48.3 mg) with stirring. The mixture was stirred for another 10 min at room temperature. After keeping the filtrate in air for 10 d, brown block-shaped crystals of (I) were formed. Complex (II) was prepared by a procedure similar to that described for (I), with $NaN_3$ replaced by $NH_4NCS$ (0.1 mmol, 7.6 mg). Brown block-shaped crystals of (II) were obtained after evaporating the solvents from the filtrate in air for 8 d.

### Compound (I)

*Crystal data*

$[Co(C_{17}H_{16}N_2O_2)(N_3)]$
$M_r = 381.28$
Orthorhombic, $Pna2_1$
$a = 11.930$ (2) Å
$b = 11.931$ (3) Å
$c = 11.225$ (2) Å
$V = 1597.7$ (6) Å$^3$
$Z = 4$
$D_x = 1.585$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 3722 reflections
$\theta = 2.5$–$27.5°$
$\mu = 1.10$ mm$^{-1}$
$T = 298$ (2) K
Block, brown
0.32 × 0.28 × 0.19 mm

*Data collection*

Bruker SMART CCD area-detector diffractometer
$\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.721$, $T_{max} = 0.819$
8835 measured reflections
3234 independent reflections
2932 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$
$\theta_{max} = 26.5°$
$h = -14 \rightarrow 14$
$k = -13 \rightarrow 14$
$l = -13 \rightarrow 14$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.130$
$S = 1.07$
3234 reflections
227 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0889P)^2 + 0.1907P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.80$ e Å$^{-3}$
$\Delta\rho_{min} = -0.42$ e Å$^{-3}$
Absolute structure: Flack (1983)
Flack parameter: 0.13 (2)

**Table 1**
Selected geometric parameters (Å, °) for (I).

| | | | |
|---|---|---|---|
| Co1—O1 | 1.874 (2) | Co1—N1 | 2.052 (3) |
| Co1—O2 | 1.899 (3) | Co1—N5$^{i}$ | 2.314 (4) |
| Co1—N2 | 2.021 (3) | Co1—N3 | 2.352 (4) |
| | | | |
| O1—Co1—O2 | 85.72 (12) | N2—Co1—N5$^{i}$ | 90.22 (15) |
| O1—Co1—N2 | 173.58 (11) | N1—Co1—N5$^{i}$ | 81.23 (13) |
| O2—Co1—N2 | 88.28 (12) | O1—Co1—N3 | 94.23 (14) |
| O1—Co1—N1 | 91.68 (12) | O2—Co1—N3 | 92.97 (14) |
| O2—Co1—N1 | 175.44 (14) | N2—Co1—N3 | 88.35 (13) |
| N2—Co1—N1 | 94.46 (12) | N1—Co1—N3 | 83.47 (12) |
| O1—Co1—N5$^{i}$ | 88.86 (15) | N5$^{i}$—Co1—N3 | 164.47 (13) |
| O2—Co1—N5$^{i}$ | 102.44 (14) | | |

Symmetry code: (i) $1 - x$, $-y$, $z + \frac{1}{2}$.

## Compound (II)

### Crystal data

$[\mathrm{Co(C_{17}H_{16}N_2O_2)(NCS)}]$
$M_r = 397.33$
Orthorhombic, $Pna2_1$
$a = 12.566$ (7) Å
$b = 11.679$ (7) Å
$c = 11.515$ (7) Å
$V = 1689.9$ (17) $\text{Å}^3$
$Z = 4$
$D_x = 1.562$ Mg m$^{-3}$

Mo $K\alpha$ radiation
Cell parameters from 2121 reflections
$\theta = 2.4$–21.8°
$\mu = 1.16$ mm$^{-1}$
$T = 298$ (2) K
Block, brown
0.33 × 0.27 × 0.21 mm

### Data collection

Bruker SMART CCD area-detector diffractometer
$\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.702$, $T_{\max} = 0.793$
9030 measured reflections

3316 independent reflections
2686 reflections with $I > 2\sigma(I)$
$R_{\mathrm{int}} = 0.060$
$\theta_{\max} = 26.5°$
$h = -15 \rightarrow 15$
$k = -14 \rightarrow 11$
$l = -14 \rightarrow 13$

### Refinement

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.129$
$S = 1.03$
3316 reflections
227 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0684P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.52$ e $\text{Å}^{-3}$
$\Delta\rho_{\min} = -0.68$ e $\text{Å}^{-3}$
Absolute structure: Flack (1983)
Flack parameter: 0.10 (3)

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

| | | | |
|---|---|---|---|
| Co1—O1 | 1.886 (3) | Co1—N1 | 2.058 (4) |
| Co1—O2 | 1.893 (3) | Co1—N3 | 2.262 (5) |
| Co1—N2 | 2.047 (4) | Co1—S1$^{\mathrm{i}}$ | 2.781 (2) |
| | | | |
| O1—Co1—O2 | 85.41 (15) | N2—Co1—N3 | 91.09 (18) |
| O1—Co1—N2 | 173.16 (14) | N1—Co1—N3 | 84.86 (18) |
| O2—Co1—N2 | 89.18 (16) | O1—Co1—S1$^{\mathrm{i}}$ | 89.96 (15) |
| O1—Co1—N1 | 91.00 (15) | O2—Co1—S1$^{\mathrm{i}}$ | 95.17 (15) |
| O2—Co1—N1 | 176.36 (14) | N1—Co1—S1$^{\mathrm{i}}$ | 84.20 (16) |
| N2—Co1—N1 | 94.35 (15) | N2—Co1—S1$^{\mathrm{i}}$ | 86.33 (16) |
| O1—Co1—N3 | 93.64 (19) | S1$^{\mathrm{i}}$—Co1—N3 | 168.54 (16) |
| O2—Co1—N3 | 95.99 (18) | | |

Symmetry code: (i) $1 - x, -y, \frac{1}{2} + z$.

All H atoms were placed in geometrically idealized positions and allowed to ride on their parent atoms, with C—H distances in the range 0.93–0.97 Å and with isotropic displacement parameters set at 1.2 times the value of the anisotropic displacement parameter of the attached atom. There were 1495 Friedel pairs measured for (I) and 1470 measured for (II).

For both compounds, data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

The author thanks Liaoning Normal University, People's Republic of China, for funding this study.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1836). Services for accessing these data are described at the back of the journal.

## References

Bhaduri, S., Tasiopoulos, A. J., Bolcar, M. A., Abbound, K. A., Streib, W. E. & Christou, G. (2003). *Inorg. Chem.* **42**, 1483–1492.
Bruker (1998). *SMART* (Version 5.628) and *SAINT* (Version 6.02). *Area Detector Control and Integration Software*. Bruker AXS Inc., Madison, Wisconsin, USA.
Dalai, S., Mukherjee, P. S., Drew, M. G. B., Lu, T.-H. & Chaudhuri, N. R. (2002). *Inorg. Chim. Acta*, **335**, 85–90.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Koner, S., Saha, S., Okamoto, K.-I. & Tuchagues, J.-P. (2003). *Inorg. Chem.* **42**, 4668–4672.
Ray, M. S., Mukhopadhyay, G., Drew, M. G. B., Lu, T.-H., Chaudhuri, S. & Ghosh, A. (2003). *Inorg. Chem. Commun.* **6**, 961–965.
Sheldrick, G. M. (1996). *SADABS. Program for Absorption Correction*. University of Göttingen, Germany.
Sheldrick, G. M. (1997*a*). *SHELXS97* and *SHELXL97*. *Programs for the Solution and Refinement of Crystal Structures*. University of Göttingen, Germany.
Sheldrick, G. M. (1997*b*). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
You, Z.-L. & Zhu, H.-L. (2004). *Acta Cryst.* C**60**, m445–m446.