

A cobalt(III) compound of a 13-membered cyclic tetraamine: *trans*-(12,12-dimethyl-1,4,7,10-tetraazacyclotetradecane)diisothiocyanatocobalt(III) tetrakisothiocyanatozinc(II) ethanol solvate

Neil F. Curtis,^{a*} Kelly Flood^b and Ward T. Robinson^b

^aSchool of Chemical and Physical Sciences, Victoria University of Wellington, Box 600, Wellington, New Zealand, and ^bChemistry Department, University of Canterbury, Christchurch, New Zealand
Correspondence e-mail: neil.curtis@vuw.ac.nz

Received 27 October 2005

Accepted 22 December 2005

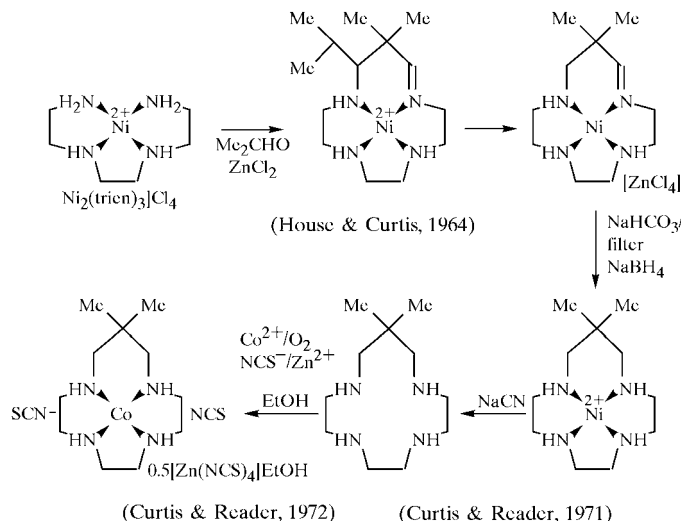
Online 31 January 2006

The title compound, [Co(NCS)₂(C₁₁H₂₆N₄)₂][Zn(NCS)₄][−]·C₂H₅OH, has two similar cations with the Co^{III} atom coordinated in a planar fashion by the 13-membered cyclic tetraamine, in the 1*R*,4*S*,7*R*,10*S* configuration, and with *trans* isothiocyanate ligands. The six-membered chelate ring is in a chair conformation, with one axially and one equatorially oriented methyl substituent [mean Co—N = 1.948 (2) Å]. The ‘opposite’ chelate ring (N⁴ and N⁷) is in an eclipsed conformation [mean Co—N = 1.928 (2) Å], and the ‘side’ chelate rings have *gauche* conformations. The mean Co—N_{NCS} distance is 1.928 (2) Å. Both cations have one Co—N—C group nearly linear and the other appreciably bent, with mean Co—N—C angles of 178.7 (1) and 160.4 (1)°, respectively. The [Zn(NCS)₄]^{2−} anion is approximately tetrahedral, with Zn—N = 1.951 (1)–1.986 (1) Å, N—Zn—N = 104.5 (1)–111.9 (1)° and Zn—N—C = 152.5 (1)–179.4 (1)°. One NH group is hydrogen bonded to the ethanol O atom and the other NH groups are bonded to thiocyanate S atoms, forming a network.

Comment

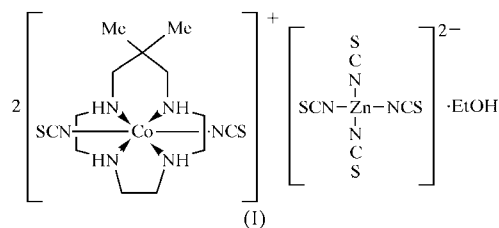
12,12-Dimethyl-1,4,7,10-tetraazacyclotetradecane (hereafter *L*) was prepared by the sequence of reactions shown in the scheme. Reaction of [Ni₂(trien)₃]Cl₂ (trien = 2,6-diazaoctane-1,8-diamine) with 2-methylpropanal (isobutyraldehyde) plus zinc chloride in methanol in a sealed tube at 413 K yields (12,12-dimethyl-1,4,7,10-tetraazacyclotrideca-13-ene)nickel(II) tetrachlorozincate instead of the anticipated 3,3-dimethyl-4-isopropyl compound, apparently by elimination of 2-methylpropene (House & Curtis, 1964). The structures of [H(*L*)]·ClO₄·H₂O (Gladkikh *et al.*, 1997) and [Ni(*L*)](ClO₄)₂ (Waters & Whittle, 1972) have been reported.

Reactions of cobalt(II) with *L* in air yield cobalt(III) compounds of *L*, isolated with a variety of additional ligands, in *cis* or *trans* configurations, depending upon the ligand and conditions (Curtis & Reader, 1972). Compounds were assigned one of three N-atom configurations from ¹H NMR



spectra. Reaction with thiocyanate forms the *trans*-[Co(NCS)₂(*L*)]⁺ cation, which was isolated as the perchlorate and tetrathiocyanatozinc(II) salts; the structure of the title compound, (I), an ethanol solvate of the latter, is now reported.

The asymmetric unit of (I) has two *trans*-[Co(NCS)₂(*L*)]⁺ cations, including Co1 (*L* with atoms N1–C13) and Co2 (*L* with atoms N21–C33), a [Zn(NCS)₄]^{2−} anion and an ethanol solvent molecule (Fig. 1). The cations have very similar azamacrocyclic conformations but slightly differing orientations of the iso-thiocyanate ligands (see below). The cations have the same 1*R*,4*S*,7*R*,10*S* configuration (the inversion centre present effects chiral balance). Atom Co1 has the NH groups N1–H and N10–H associated with the six-membered chelate ring on the same side of the CoN₄ plane as the axial methyl substituent C121, and groups N4–H and N7–H on the opposite side, with an analogous arrangement for Co2.



For both cations, the Co—N_{amine} distances are longer for the N atoms of the six-membered chelate ring, which has an axially oriented methyl substituent [mean value = 1.948 (2) Å], than for the opposite five-membered chelate ring, which has a strained eclipsed conformation [mean value = 1.928 (2) Å], with mean Co—N_{NCS} = 1.896 (2) Å (Table 1). For both cations, one isothiocyanate group is close to being linear and the other is appreciably bent; for Co1, atom S45 (on the side opposite to the axial methyl group C122) is

angled towards N1, while for Co2, atom S56 (on the same side as the axial methyl group C222) is angled towards C26.

The N₄ groups of both macrocycles are coplanar to within 0.006 (1) Å, with the N₄ planes of the two cations inclined at 59.2 (4)°. The six-membered chelate rings have chair conformations (N—Co—N *ca* 97°), with methyl groups C121 and C321 equatorial and C122 and C322 axial. Adjacent five-membered chelate rings have *gauche* conformations (N—Co—N *ca* 89°) and the 'opposite' rings have eclipsed conformations (N—Co—N *ca* 84°). The same configuration and similar conformations are present for [Ni(L)](ClO₄)₂ and a similar arrangement is present for [H(L)]ClO₄·H₂O. The displacements in Å (s.u. 0.002 Å, unless shown) of atoms from the respective N₄ planes (the first value is for Co1 and the second is the equivalent value for Co2) are: C1 -0.015 (1) and -0.022 (1); C2 -0.302 and -0.380; C3 0.426 and 0.347; C5 0.783 and 0.903; C6 0.810 and 0.792; C8 0.435 and 0.418; C9 -0.327 and -0.314; C11 -0.846 and -0.834; C12 -0.516 and -0.493; C13 -0.835 and -0.827; C121 -1.438 (3) and -1.408 (3); C122 0.951 and 0.977.

The tetraisothiocyanatozinc(II) anion is approximately tetrahedral, with Zn—N distances in the range 1.951 (1)–1.986 (1) Å, N—Zn—N angles in the range 104.5 (1)–111.9 (1)° and C—N—C angles in the range 152.5 (1)–179.3 (1)°.

An extensive hydrogen-bonding network is present (Table 2). Ethanol atom O40 forms hydrogen bonds with the N24—H group, while all other NH groups form hydrogen bonds with thiocyanate S atoms.

cis-Chloro(12-methyl-1,4,7,10-tetraazacyclotridecan-12-amine)-cobalt(III) tetrachlorocobaltate(II) methanol solvate, which has the cyclic amine in a folded conformation for which 'hole-size' constraints were relaxed, has Co—N_{ring} distances for two cations in the range 1.925 (7)–1.985 (7) Å, with a mean of 1.95 Å (Lawrance *et al.*, 1992).

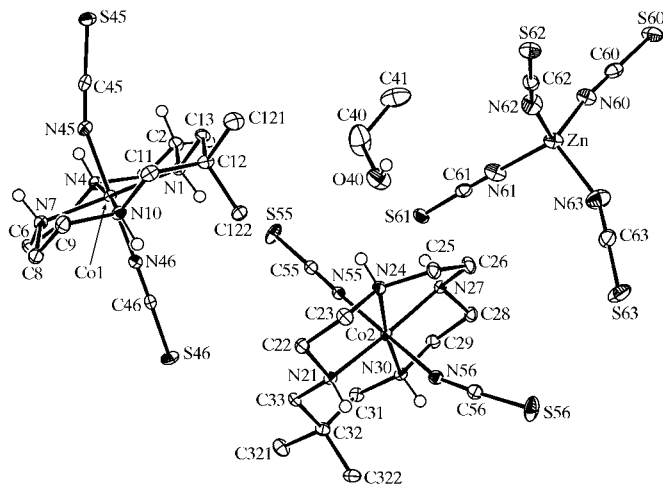


Figure 1

The structure of (I), with displacement ellipsoids drawn at the 50% probability level. H atoms bonded to C atoms have been omitted for clarity, and H atoms bonded to N or O atoms are shown as circles of arbitrary radii.

Dimensions for related compounds are shown in Table 3. The Co—N_{amine} distances for [Co(NCS)₂(L)][Zn(NCS)₄]₂·EtOH are significantly shorter than for the related compounds, which have acyclic or 14-membered tetraaza-macrocyclic ligands. This shortening can be attributed to the 'hole size' effect, with the smaller strain-free cavity of the 13-membered cyclic amine effectively constricting the Co—N distances. Alternatively, and more plausibly, the lower number of metal–ligand and intra-ligand repulsive interactions for the 13-membered cyclic amine permit the Co—N distances to approach more closely their hypothetical strain-free values.

The isothiocyanate groups of these compounds have Co—N—C angles either approximately linear or appreciably bent, although this angle does not correlate with any significant variation in the Co—N distance. Several of the related compounds, including the title compound, have thiocyanate groups of both types. For the title compound, bending of the NCS[−] ion does not correlate with the location of the axial methyl substituent.

Experimental

The cyclic amine *L* was prepared as reported by House & Curtis (1964) and Curtis & Reader (1971). [Co(NCS)₂(L)][Zn(NCS)₄]₂·EtOH was prepared from this and crystallized as reported by Curtis & Reader (1972).

Crystal data

[Co(NCS)₂(C₁₁H₂₆N₄)₂]₂·
[Zn(NCS)₄]₂·C₂H₆O
*M*_r = 1122.66
Triclinic, *P*1
a = 9.9776 (6) Å
b = 14.0647 (8) Å
c = 19.586 (1) Å
α = 70.511 (2)°
β = 82.199 (2)°
γ = 71.989 (2)°
V = 2462.5 (2) Å³

Z = 2
*D*_x = 1.523 Mg m^{−3}
Mo *Kα* radiation
Cell parameters from 9916
reflections
θ = 1.1–32.3°
μ = 1.54 mm^{−1}
T = 273 (2) K
Block, orange
0.6 × 0.4 × 0.4 mm

Data collection

Bruker SMART CCD area-detector
diffractometer
φ and *ω* scans
Absorption correction: multi-scan
(SADABS, Version 2.03;
Blessing, 1995)
*T*_{min} = 0.396, *T*_{max} = 0.540
51668 measured reflections

14587 independent reflections
13265 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.024
*θ*_{max} = 32.3°
h = −12 → 14
k = −18 → 20
l = −19 → 28

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.024
wR(*F*²) = 0.064
S = 0.88
14587 reflections
547 parameters
H-atom parameters constrained

w = 1/[σ²(*F*_o²) + (0.0375*P*)²
+ 1.5995*P*]
where *P* = (*F*_o² + 2*F*_c²)/3
(Δ/σ)_{max} = 0.002
Δρ_{max} = 0.82 e Å^{−3}
Δρ_{min} = −0.61 e Å^{−3}

All H atoms were included in calculated positions, using the riding model, with C—H bond lengths ranging from 0.96 to 0.97 Å, N—H bond lengths of 0.91 Å and O—H bond lengths of 0.82 Å, and with *U*_{iso}(H) = 1.2*U*_{eq}(C,N) or 1.5*U*_{eq}(O).

Table 1
Selected geometric parameters (Å, °).

Co1—N45	1.901 (1)	Co2—N27	1.935 (1)
Co1—N46	1.903 (1)	Co2—N21	1.950 (1)
Co1—N4	1.926 (1)	Co2—N30	1.951 (1)
Co1—N7	1.931 (1)	N21—C33	1.487 (2)
Co1—N1	1.952 (1)	N55—C55	1.169 (2)
Co1—N10	1.954 (1)	N56—C56	1.168 (2)
N45—C45	1.171 (2)	C55—S55	1.633 (1)
N46—C46	1.169 (2)	C56—S56	1.625 (1)
C45—S45	1.627 (1)	Zn1—N62	1.952 (1)
C46—S46	1.625 (1)	Zn1—N60	1.957 (1)
Co2—N55	1.903 (1)	Zn1—N63	1.972 (1)
Co2—N56	1.904 (1)	Zn1—N61	1.990 (1)
Co2—N24	1.933 (1)		
N45—Co1—N46	179.51 (5)	N55—Co2—N56	179.53 (4)
N45—Co1—N4	89.21 (4)	N55—Co2—N24	89.68 (4)
N46—Co1—N4	90.77 (4)	N56—Co2—N24	90.77 (4)
N45—Co1—N7	90.42 (4)	N55—Co2—N27	89.68 (4)
N46—Co1—N7	90.07 (4)	N56—Co2—N27	90.54 (4)
N4—Co1—N7	84.98 (4)	N24—Co2—N27	83.89 (4)
N45—Co1—N1	90.78 (4)	N55—Co2—N21	91.18 (4)
N46—Co1—N1	88.73 (4)	N56—Co2—N21	88.66 (4)
N4—Co1—N1	88.91 (4)	N24—Co2—N21	89.31 (4)
N7—Co1—N1	173.75 (4)	N27—Co2—N21	173.14 (4)
N45—Co1—N10	91.31 (4)	N55—Co2—N30	91.81 (4)
N46—Co1—N10	88.77 (4)	N56—Co2—N30	87.77 (4)
N4—Co1—N10	174.08 (4)	N24—Co2—N30	173.22 (4)
N7—Co1—N10	89.12 (4)	N27—Co2—N30	89.50 (4)
N1—Co1—N10	96.98 (4)	N21—Co2—N30	97.27 (4)
C45—N45—Co1	158.7 (1)	C55—N55—Co2	177.8 (1)
C46—N46—Co1	178.8 (1)	C56—N56—Co2	162.0 (1)
N45—C45—S45	177.4 (1)	N55—C55—S55	178.5 (1)
N46—C46—S46	179.0 (1)	N56—C56—S56	176.4 (1)

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...S55	0.91	2.61	3.398 (1)	146
N4—H4...S62 ⁱ	0.91	2.54	3.391 (1)	156
N7—H7...S45 ⁱⁱ	0.91	2.59	3.308 (1)	136
N10—H10...S61 ⁱⁱⁱ	0.91	2.69	3.439 (1)	140
N21—H21...S56 ^{iv}	0.91	2.62	3.361 (1)	139
N24—H24...O40	0.91	2.19	2.932 (2)	138
N27—H27...S61	0.91	2.97	3.712 (1)	140
N30—H30...S63 ^v	0.91	2.61	3.330 (1)	137
O40—H40...S60 ⁱⁱⁱ	0.82	2.56	3.377 (1)	174

Symmetry codes: (i) *x*, *y* − 1, *z*; (ii) −*x*, −*y*, −*z*; (iii) *x* − 1, *y*, *z*; (iv) −*x*, −*y* + 1, −*z* + 1; (v) −*x* + 1, −*y* + 1, −*z* + 1.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINTE* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics:

Table 3
Selected dimensions (Å, °) for analogous compounds.

Compound	Mean Co—N _{amine}	Mean Co—N _{NCS}	Co—N _{NCS} —C [†]	Co—N _{NCS} —C [‡]
(I)	1.938 (3)	1.928 (2)	178.7 (1)	160.4 (1)
(II)	1.946 (1)	1.896 (1)	175.9 (1)§	168.3 (1)¶
(III)	1.981 (3)	1.975 (3)		167.0 (3)
(IV)	1.976 (4)	1.883 (3)		167 (3)
(V)	1.970 (6)	1.905 (6)	176.3 (5)	141.7 (3)

[†] Near-linear Co—N—C. [‡] Appreciably bent Co—N—C. [§] Centrosymmetric cation. [¶] Twofold symmetrical cation. Notes: (I) is *trans*-(12,12-dimethyl-1,4,7,10-tetraazacyclotetradecane)diisothiocyanatocobalt(III) tetraisothiocyanatozinc(II) ethanol solvate (this work), (II) is *trans*-bis(ethane-1,2-diamine)di(isothiocyanato)cobalt(III) thiocyanate (two cations, one centrosymmetric and the other with twofold symmetry, both with similar Co—N distances; Liu *et al.*, 1995), (III) is (−)-589-*trans*-SS-(3,6-diazaoctane-1,8-diamine)di(isothiocyanato)cobalt(III) μ -(+)-tartrato(4−)- μ -(+)-hydrogentartrato(3−)diantimonate(III) tetrahydrate (Kushi *et al.*, 1983), (IV) is *trans*-(1,4,8,11-tetraazacyclotetradeca-4,11-diene)bis(isothiocyanato)cobalt(III) thiocyanate (two centrosymmetric cations; Burgess *et al.*, 1999) and (V) is *trans*-(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)bis(isothiocyanato)cobalt(III) thiocyanate [mean Co—N_{imine} = 1.930 (6) Å; Lu *et al.*, 1996].

ORTEP-3.2 (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ1078). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
 Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
 Bruker (1997). *SMART* and *SAINTE*. Versions 6.14. Bruker AXS Inc., Madison, Wisconsin, USA.
 Burgess, J., Fawcett, J., Haines, R. I., Singh, K. & Russell, D. R. (1999). *Transition Met. Chem.* **24**, 355–361.
 Curtis, N. F. & Reader, G. W. (1971). *J. Chem. Soc. Dalton Trans.* pp. 1771–1777.
 Curtis, N. F. & Reader, G. W. (1972). *J. Chem. Soc. Dalton Trans.* pp. 1457–1460.
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
 Gladkikh, O. P., Curtis, N. F. & Turnbull, M. M. (1997). *Acta Cryst.* **C53**, 586–587.
 House, D. A. & Curtis, N. F. (1964). *J. Am. Chem. Soc.* **86**, 1331–1341.
 Kushi, Y., Kuramoto, M., Utsuno, S. & Yoneda, H. (1983). *Bull. Chem. Soc. Jpn.* **56**, 2742–2747.
 Lawrance, G. A., Manning, T. M., Maeder, M., Martinez, M., O’Leary, M. A., Patalinghug, W. C., Skelton, B. W. & White, A. H. (1992). *J. Chem. Soc. Dalton Trans.* pp. 1635–1641.
 Liu, Y.-H., Fronczek, F. R., Watkins, S. F., Shaffer, G. W. & Musselman, R. L. (1995). *Acta Cryst.* **C51**, 1992–1994.
 Lu, T.-H., Tahirov, T. H., Chen, B.-H., Lai, C.-Y. & Chung, C.-S. (1996). *Acta Cryst.* **C52**, 2684–2687.
 Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
 Siemens (1995). *SMART* and *SAINTE*. Versions 4.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
 Waters, J. M. & Whittle, K. R. (1972). *J. Inorg. Nucl. Chem.* **34**, 155–161.