

Triazidocobalt(III) complexes with tridentate amine ligands

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The title compounds, $[N-(2\text{-aminoethyl})\text{-}1,3\text{-propanediamine-}\kappa^3N]\text{triazidocobalt(III)}$, $[\text{Co}(\text{N}_3)_3(\text{C}_5\text{H}_{15}\text{N}_3)]$, $[N-(2\text{-aminoethyl})\text{-}N\text{-methyl-}1,3\text{-propanediamine-}\kappa^3N]\text{triazidocobalt(III)}$, $[\text{Co}(\text{N}_3)_3(\text{C}_6\text{H}_{17}\text{N}_3)]$, $[N-(2\text{-aminopropyl})\text{-}1,3\text{-propanediamine-}\kappa^3N]\text{triazidocobalt(III)}$, $[\text{Co}(\text{N}_3)_3(\text{C}_6\text{H}_{17}\text{N}_3)]$, and $[N-(2\text{-aminopropyl})\text{-}N\text{-methyl-}1,3\text{-propanediamine-}\kappa^3N]\text{triazidocobalt(III)}$, $[\text{Co}(\text{N}_3)_3(\text{C}_7\text{H}_{19}\text{N}_3)]$, each consist of a Co^{III} atom, three azide ligands in a meridional configuration and a tridentate amine ligand, namely aepn $[N-(2\text{-aminoethyl})\text{-}1,3\text{-propanediamine}]$ or dpt $[N-(3\text{-aminopropyl})\text{-}1,3\text{-propanediamine}]$, or their N -methylated analogs.

Comment

The title compounds, (I)–(IV) (Fig. 1), were studied as part of our investigation of the crystallization behavior of neutral Co^{III} complexes. Our specific point of interest was to prepare a series of compounds with similar molecular geometry and compare their molecular packing structures in order to discover whether intermolecular hydrogen bonding plays a role in their crystallization pathways. For example, both facial (Lukaszewski *et al.*, 1976) and meridional (Druding & Sancilio, 1974) isomers of $\text{Co}(\text{dien})(\text{N}_3)_3$ (dien is diethylenetriamine) crystallize as typical racemates; however, a closely related compound, $\text{Mn}(\text{tacn})(\text{N}_3)_3$ (tacn is 1,4,7-triazacyclononane) (Wieghardt *et al.*, 1987) has been known to crystallize as a conglomerate in space group

$P2_12_12_1$. No decisive information in that regard could be obtained from the structures of the four title compounds, since they all crystallized in centrosymmetric space groups. However, analyses of the molecular packing suggest that the alignment of the azide ligands with the $-\text{NH}_2$ H atoms of the amine ligands provides a good opportunity for intermolecular interactions between heterochiral molecules, as the packing

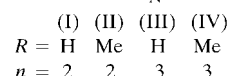
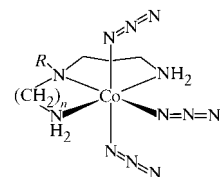


diagram (Fig. 2) of compound (III) shows. In the figure, two H atoms of an $-\text{NH}_2$ moiety of the dpt ligand form hydrogen bonds with azide N atoms of two adjacent molecules [$d(\text{H} \cdots \text{N}) = 2.27(3)$ and $2.27(2)$ Å], and crystallographic inversion symmetry is imposed on such contacts at the center of each unit-cell face. Meanwhile, the tacn ligand of $\text{Mn}(\text{tacn})(\text{N}_3)_3$ has only a secondary nitrogen ($-\text{NH}-$) which has one H atom available for hydrogen bonding and therefore limits the chance of azide N atoms to form 'racemic inter-

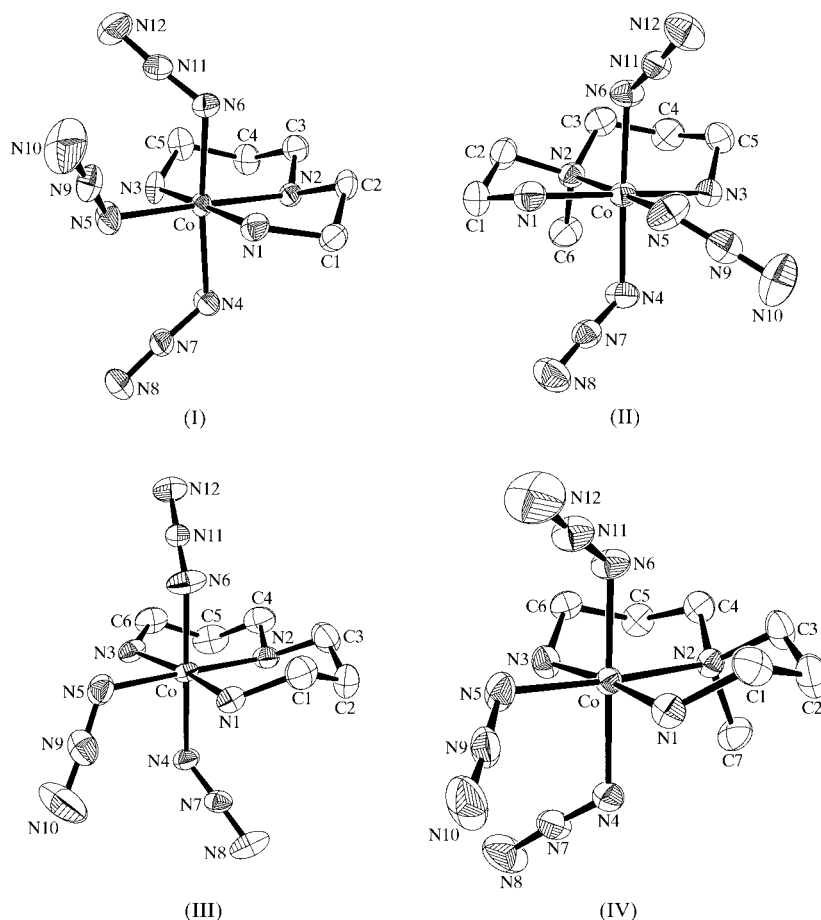


Figure 1
ORTEP (Burnett & Johnson, 1996) views of compounds (I)–(IV) showing the labeling of the non-H atoms. Displacement ellipsoids are drawn at probability levels of 50% for (I)–(III) and 40% for (IV).

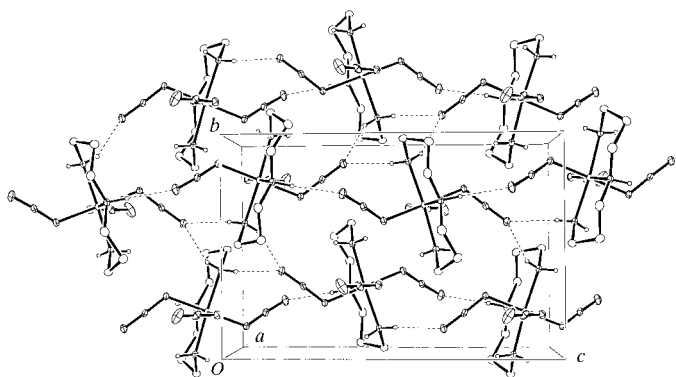


Figure 2

Perspective view of the molecular packing of compound (III). Dashed lines represent hydrogen-bonded interactions. Carbon-bound H atoms have been omitted for clarity.

actions'. The packing structures of the other three compounds will not be discussed here since they can be understood in the same context as the above. Note that the tacn ligand of $\text{Mn}(\text{tacn})(\text{N}_3)_3$ does not have a primary nitrogen with two H atoms available for hydrogen bonding.

The geometry of the coordinated azide groups in the four triazidocobalt(III) complexes are in good agreement with known values (Dori & Ziolo, 1973). For example, the average distance between the middle and terminal nitrogens [1.140 (3)–1.165 (7) Å] of the azide groups are slightly shorter than the distance between the middle and metal-bound N atom [1.182 (2)–1.207 (6) Å]. For the angular geometry, the Co–N–N angles are close to 120° with the exception of Co–N6–N11 of compound (III) [126.9 (2)°]. The N–N–N angles fall between 175.5 (2) and 178.0 (2)°.

The three Co–N distances associated with the chelating amine ligands are not quite uniform, with the Co–N1 bond being the shortest and Co–N2 being the longest in compounds (I), (II) and (IV). In most cases, the differences are statistically significant. Meanwhile, the differences in the three Co–N distances involving the azide ligands are much smaller, with a maximum variation of 0.03 Å in compound (III). The only notable deviation for the angular geometry around the Co atom is the angle N1–Co–N3 of compound (III) [168.96 (8)°], which is a consequence of forming two six-membered chelate rings with the dpt ligand. In compound (IV), where the dpt ligand has an additional methyl group on its secondary nitrogen (N2), the same angle is 172.86 (8)° because the Co atom makes a longer bond to N2 than in compound (III).

Experimental

Compounds (I), (II) and (IV) were prepared by conventional air-oxidation of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in the presence of the corresponding amine ligand. NaN_3 was added in portions during the aeration. Compound (III) was obtained by mixing NaN_3 with $\text{Co}(\text{dpt})\text{Cl}_3$ (Barefield *et al.*, 1980) in water. The Me-aepn ligand used in the preparation of (II) was synthesized by the reaction of 2-bromoethylamine hydrobromide with *N*-methyl-1,3-propanediamine in isopropyl alcohol. Single

crystals for data collection were obtained by recrystallization from water for (I), acetonitrile for (II) and (III), and acetone for (IV). Analysis found (calculated) for (I): C 19.35 (19.87), H 5.19 (5.00), N 55.06 (55.62)%; (II): C 22.72 (22.79), H 5.35 (5.42), N 52.87 (53.15)%; (III): C 22.55 (22.79), H 5.76 (5.42), N 52.62 (53.15)%; (IV): C 24.81 (25.45), H 6.13 (5.81), N 50.59 (50.90)%.

Compound (I)

Crystal data

$[\text{Co}(\text{N}_3)_3(\text{C}_5\text{H}_{15}\text{N}_3)]$
 $M_r = 302.22$
 Monoclinic, $P2_1/n$
 $a = 8.795$ (4) Å
 $b = 15.958$ (5) Å
 $c = 8.903$ (4) Å
 $\beta = 106.78$ (5)°
 $V = 1196.4$ (9) Å³
 $Z = 4$

$D_x = 1.678$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 6.47$ – 15.10 °
 $\mu = 1.442$ mm⁻¹
 $T = 293$ K
 Brick, dark green
 $0.49 \times 0.20 \times 0.18$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω - 2θ scans
 Absorption correction: ψ scan
 (NRCVAX ABSORP; Gabe *et al.*, 1989)
 $T_{\min} = 0.456$, $T_{\max} = 0.771$
 2494 measured reflections
 2342 independent reflections

1370 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.042$
 $\theta_{\text{max}} = 26.00$ °
 $h = -10 \rightarrow 10$
 $k = 0 \rightarrow 19$
 $l = 0 \rightarrow 10$
 3 standard reflections
 frequency: 240 min
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.052$
 $wR(F^2) = 0.125$
 $S = 1.139$
 2342 reflections
 223 parameters

All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.0891P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 1.71$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.71$ e Å⁻³

Table 1

Selected geometric parameters (Å, °) for (I).

Co–N6	1.943 (4)	N4–N7	1.202 (6)
Co–N5	1.954 (4)	N5–N9	1.193 (6)
Co–N1	1.955 (5)	N6–N11	1.207 (6)
Co–N4	1.963 (4)	N7–N8	1.153 (7)
Co–N3	1.970 (5)	N9–N10	1.165 (7)
Co–N2	1.971 (4)	N11–N12	1.141 (7)
N6–Co–N5	92.7 (2)	N9–N5–Co	119.3 (4)
N6–Co–N4	174.5 (2)	N11–N6–Co	121.3 (4)
N5–Co–N4	91.8 (2)	N8–N7–N4	176.9 (6)
N1–Co–N3	178.4 (2)	N10–N9–N5	176.5 (6)
N5–Co–N2	178.3 (2)	N12–N11–N6	176.1 (5)
N7–N4–Co	120.4 (4)		

Compound (II)

Crystal data

$[\text{Co}(\text{N}_3)_3(\text{C}_6\text{H}_{17}\text{N}_3)]$
 $M_r = 316.25$
 Monoclinic, $P2_1/n$
 $a = 8.560$ (3) Å
 $b = 9.404$ (2) Å
 $c = 16.149$ (4) Å
 $\beta = 91.65$ (3)°
 $V = 1299.5$ (7) Å³
 $Z = 4$

$D_x = 1.616$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 8.14$ – 12.65 °
 $\mu = 1.331$ mm⁻¹
 $T = 293$ K
 Brick, dark green
 $0.50 \times 0.48 \times 0.21$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer	1851 reflections with $I > 2\sigma(I)$
ω -2 θ scans	$R_{\text{int}} = 0.019$
Absorption correction: ψ scan (<i>NRCVAX ABSORP</i> ; Gabe <i>et al.</i> , 1989)	$\theta_{\text{max}} = 24.97^\circ$
$T_{\text{min}} = 0.654$, $T_{\text{max}} = 0.756$	$h = -10 \rightarrow 10$
2357 measured reflections	$k = 0 \rightarrow 11$
2278 independent reflections	$l = 0 \rightarrow 19$
	3 standard reflections
	frequency: 240 min
	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0364P)^2 + 0.0998P]$
$R[F^2 > 2\sigma(F^2)] = 0.022$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.057$	$(\Delta/\sigma)_{\text{max}} = -0.009$
$S = 1.118$	$\Delta\rho_{\text{max}} = 0.34 \text{ e } \text{\AA}^{-3}$
2278 reflections	$\Delta\rho_{\text{min}} = -0.22 \text{ e } \text{\AA}^{-3}$
240 parameters	
All H-atom parameters refined	

Table 2

Selected geometric parameters (\AA , $^\circ$) for (II).

Co–N6	1.953 (2)	N4–N7	1.203 (2)
Co–N1	1.954 (2)	N5–N9	1.186 (3)
Co–N5	1.955 (2)	N6–N11	1.196 (2)
Co–N3	1.964 (2)	N7–N8	1.150 (2)
Co–N4	1.966 (2)	N9–N10	1.144 (3)
Co–N2	2.032 (2)	N11–N12	1.149 (2)
N6–Co–N5	89.73 (7)	N9–N5–Co	120.93 (15)
N1–Co–N3	177.15 (8)	N11–N6–Co	122.11 (13)
N6–Co–N4	178.11 (7)	N8–N7–N4	177.4 (2)
N5–Co–N4	89.17 (8)	N10–N9–N5	176.7 (2)
N5–Co–N2	173.73 (7)	N12–N11–N6	175.5 (2)
N7–N4–Co	118.58 (13)		

Compound (III)

Crystal data

$[\text{Co}(\text{N}_3)_3(\text{C}_6\text{H}_7\text{N}_3)]$	$D_x = 1.628 \text{ Mg m}^{-3}$
$M_r = 316.25$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25 reflections
$a = 9.8040 (12) \text{ \AA}$	$\theta = 7.94$ – 12.80°
$b = 9.286 (2) \text{ \AA}$	$\mu = 1.341 \text{ mm}^{-1}$
$c = 14.209 (2) \text{ \AA}$	$T = 293 \text{ K}$
$\beta = 94.267 (14)^\circ$	Brick, dark green
$V = 1290.1 (3) \text{ \AA}^3$	$0.65 \times 0.45 \times 0.35 \text{ mm}$
$Z = 4$	

Data collection

Enraf–Nonius CAD-4 diffractometer	1918 reflections with $I > 2\sigma(I)$
ω -2 θ scans	$R_{\text{int}} = 0.027$
Absorption correction: ψ scan (<i>NRCVAX ABSORP</i> ; Gabe <i>et al.</i> , 1989)	$\theta_{\text{max}} = 26.46^\circ$
$T_{\text{min}} = 0.570$, $T_{\text{max}} = 0.625$	$h = -12 \rightarrow 12$
2777 measured reflections	$k = 0 \rightarrow 11$
2664 independent reflections	$l = 0 \rightarrow 17$
	3 standard reflections
	frequency: 240 min
	intensity decay: none

Refinement

Refinement on F^2	All H-atom parameters refined
$R[F^2 > 2\sigma(F^2)] = 0.025$	$w = 1/[\sigma^2(F_o^2) + (0.0326P)^2]$
$wR(F^2) = 0.060$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.139$	$(\Delta/\sigma)_{\text{max}} = 0.004$
2664 reflections	$\Delta\rho_{\text{max}} = 0.31 \text{ e } \text{\AA}^{-3}$
240 parameters	$\Delta\rho_{\text{min}} = -0.23 \text{ e } \text{\AA}^{-3}$

Table 3

Selected geometric parameters (\AA , $^\circ$) for (III).

Co–N6	1.943 (2)	N4–N7	1.196 (2)
Co–N3	1.970 (2)	N5–N9	1.196 (3)
Co–N5	1.973 (2)	N6–N11	1.182 (2)
Co–N4	1.976 (2)	N7–N8	1.155 (2)
Co–N1	1.981 (2)	N9–N10	1.145 (3)
Co–N2	2.010 (2)	N11–N12	1.160 (3)
N6–Co–N5	89.37 (8)	N9–N5–Co	118.57 (14)
N6–Co–N4	179.40 (8)	N11–N6–Co	126.9 (2)
N5–Co–N4	91.16 (8)	N8–N7–N4	178.0 (2)
N3–Co–N1	168.96 (8)	N10–N9–N5	176.6 (2)
N5–Co–N2	178.20 (8)	N12–N11–N6	176.5 (2)
N7–N4–Co	119.82 (14)		

Compound (IV)

Crystal data

$[\text{Co}(\text{N}_3)_3(\text{C}_7\text{H}_9\text{N}_3)]$	$Z = 2$
$M_r = 330.27$	$D_x = 1.579 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.848 (5) \text{ \AA}$	Cell parameters from 25 reflections
$b = 8.931 (2) \text{ \AA}$	$\theta = 8.41$ – 13.54°
$c = 9.606 (3) \text{ \AA}$	$\mu = 1.249 \text{ mm}^{-1}$
$\alpha = 105.98 (2)^\circ$	$T = 293 \text{ K}$
$\beta = 90.51 (4)^\circ$	Polyhedra, dark green
$\gamma = 106.99 (3)^\circ$	$0.45 \times 0.38 \times 0.18 \text{ mm}$
$V = 694.6 (5) \text{ \AA}^3$	

Data collection

Enraf–Nonius CAD-4 diffractometer	2066 reflections with $I > 2\sigma(I)$
ω -2 θ scans	$\theta_{\text{max}} = 24.98^\circ$
Absorption correction: ψ scan (<i>NRCVAX ABSORP</i> ; Gabe <i>et al.</i> , 1989)	$h = -10 \rightarrow 10$
$T_{\text{min}} = 0.666$, $T_{\text{max}} = 0.799$	$k = 0 \rightarrow 10$
2447 measured reflections	$l = -11 \rightarrow 10$
2447 independent reflections	3 standard reflections
	frequency: 240 min
	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0397P)^2 + 0.1912P]$
$R[F^2 > 2\sigma(F^2)] = 0.026$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.066$	$(\Delta/\sigma)_{\text{max}} = 0.024$
$S = 1.125$	$\Delta\rho_{\text{max}} = 0.32 \text{ e } \text{\AA}^{-3}$
2447 reflections	$\Delta\rho_{\text{min}} = -0.27 \text{ e } \text{\AA}^{-3}$
257 parameters	
All H-atom parameters refined	

Table 4

Selected geometric parameters (\AA , $^\circ$) for (IV).

Co–N6	1.951 (2)	N4–N7	1.192 (3)
Co–N5	1.958 (2)	N5–N9	1.203 (3)
Co–N4	1.974 (2)	N6–N11	1.195 (3)
Co–N1	1.976 (2)	N7–N8	1.152 (3)
Co–N3	1.982 (2)	N9–N10	1.140 (3)
Co–N2	2.083 (2)	N11–N12	1.144 (3)
N6–Co–N5	89.89 (9)	N9–N5–Co	119.6 (2)
N6–Co–N4	177.20 (8)	N11–N6–Co	118.8 (2)
N5–Co–N4	89.51 (9)	N8–N7–N4	176.9 (3)
N1–Co–N3	172.86 (8)	N10–N9–N5	177.2 (2)
N5–Co–N2	175.41 (8)	N12–N11–N6	176.6 (3)
N7–N4–Co	120.9 (2)		

Relatively large residual electron density found in the final difference map of (I) was ignored since it was too close to the Co atom ($<1.0 \text{ \AA}$). The N–H distances are in the range 0.75 (6)–

0.91 (6) Å and the C–H distances are in the range 0.85 (6)–1.04 (3) Å.

For all compounds, data collection: *CAD-4-PC Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4-PC Software*; data reduction: *NRCVAX DATRD2* (Le Page & Gabe, 1979); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1147). Services for accessing these data are described at the back of the journal.

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