

Conformational isomers of neutral  
*trans*-dinitrocobalt(III) complexes

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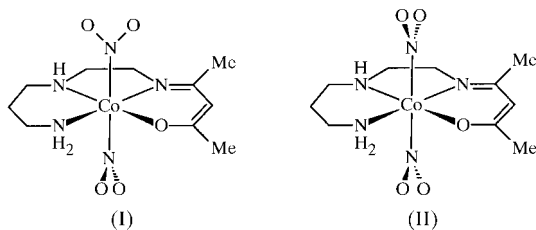
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The reaction of  $\text{Co}(\text{acac})_3$  with *N*-(2-aminoethyl)-1,3-propanediamine in the presence of  $\text{NaNO}_2$  results in the preparation of an unexpected dinitrocobalt(III) compound, (11-amino-4-methyl-5,8-diazaundeca-2,4-dien-2-olato- $\kappa^4\text{N}^{5,8,11},\text{O}$ )-dinitrocobalt(III),  $[\text{Co}(\text{C}_{10}\text{H}_{20}\text{N}_3\text{O})(\text{NO}_2)_2]$ , containing the tetradentate anion of 11-amino-4-methyl-5,8-diazaundeca-2,4-dien-2-ol. Two isomers of the compound were obtained by recrystallization of the crude product. In one isomer, the two *trans* nitro groups are staggered, and in the other they are eclipsed.

## Comment

Tris(acetylacetonato)cobalt(III),  $\text{Co}(\text{acac})_3$ , is a useful starting material for the preparation of various  $\text{Co}^{\text{III}}$  complexes. Although the same is true for the anionic complex  $[\text{Co}(\text{CO}_3)_3]^{3-}$ ,  $\text{Co}(\text{acac})_3$  has an advantage when there is a need for using organic solvents for the reaction. Also, a coordinated acac ligand can undergo an organic reaction with nucleophilic reagents to generate a new chelating ligand.

The title compounds, (I) (Fig. 1) and (II) (Fig. 2), were obtained while trying to prepare trinitrocobalt(III) complexes with facial configurations by replacing the acac ligands of  $\text{Co}(\text{acac})_3$  with a tridentate amine ligand and nitro groups. Instead, a condensation reaction occurred between an  $\text{NH}_2$  group of the amine ligand and a carbonyl group of a coordinated acac ligand to give the monoanionic tetradentate ligand.



Compound (I) has two nitro groups in a staggered conformation [ $\text{O}2-\text{N}4 \cdots \text{N}5-\text{O}5 = 63.7 (2)^\circ$ ] and appears to be less soluble than compound (II), in which the two nitro groups are almost eclipsed [ $\text{O}2-\text{N}4 \cdots \text{N}5-\text{O}5 = 13.3 (5)^\circ$ ]. A similar case is known in which two conformational isomers of *mer*- $[\text{Co}(\text{en})(\text{NH}_3)(\text{NO}_2)_3]$  crystallize with different crystal habits

and color (brown and yellow), but in the same space group ( $P2_1/c$ ) (Jensen *et al.*, 1970).

The geometry of the tetradentate ligand around the Co atom is quite similar in both structures. For example,  $\text{N}1-\text{C}4$  [1.298 (3) Å for (I); 1.294 (5) Å for (II)] and  $\text{C}2-\text{C}3$  [1.367 (4) Å for (I); 1.362 Å for (II)] are considered as double bonds, and the single negative charge is mostly assigned to O1 since the  $\text{O}1-\text{C}2$  bond [1.289 (3) Å for (I); 1.293 (4) Å for (II)] is rather long for a carbonyl group. Also, the relatively short distance of  $\text{Co}-\text{O}1$  [1.889 (2) Å for (I); 1.880 (3) Å for (II)] reflects an anionic character of the ligand atom. The distances between cobalt and the  $\text{NO}_2$  atoms of (I) are uneven with the difference being  $20\sigma$ ; in (II), the difference is only  $4\sigma$ . No severe distortion is observed in the angular geometry around the octahedral Co atom. The four N—O bond distances in the two nitro groups of (II) fall within the  $3\sigma$  range, with an average of 1.226 (4) Å. In (I),  $\text{N}4-\text{O}2$  [1.252 (3) Å] is significantly longer than the other three N—O bonds whose average is 1.226 (2) Å, probably because of the short intramolecular contact between O2 and the H atom on N2 [1.993 (24) Å].

In the packing structure of (I) (Fig. 3), the two nitro groups, staggered with respect to each other, form hydrogen bonds with  $\text{NH}_2$  H atoms of neighboring molecules related by inversion symmetry. This one-dimensional interaction extends along the *c* direction of the unit cell, and no other hydrogen

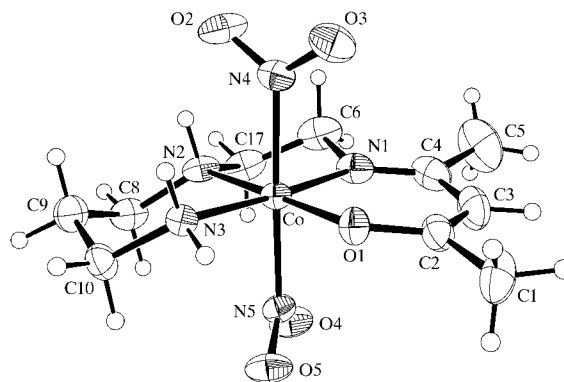


Figure 1  
ORTEP (Burnett & Johnson, 1996) view of (I) with displacement ellipsoids drawn at the 40% probability level.

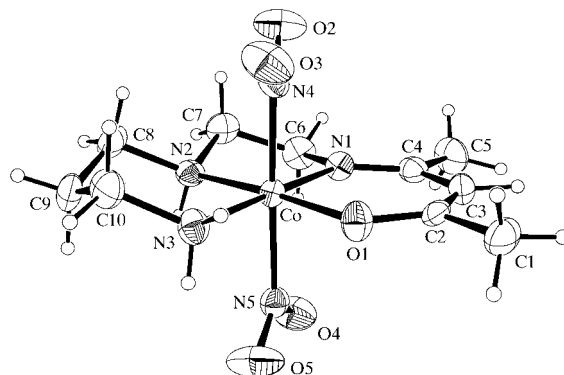
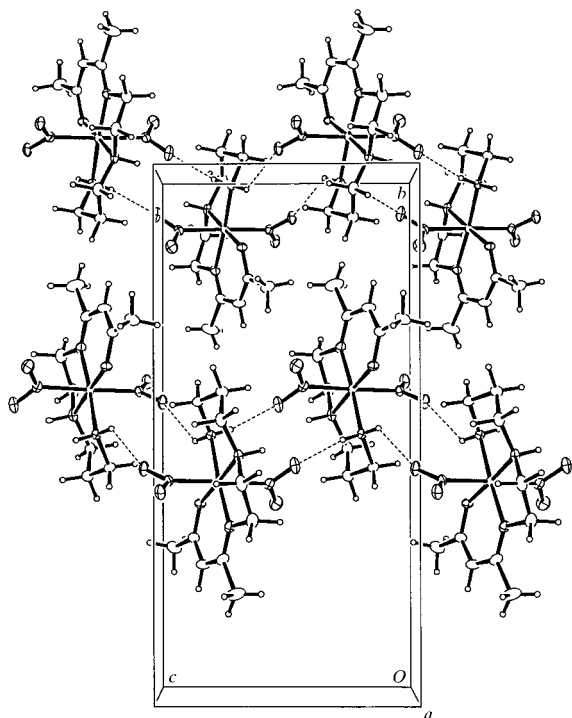
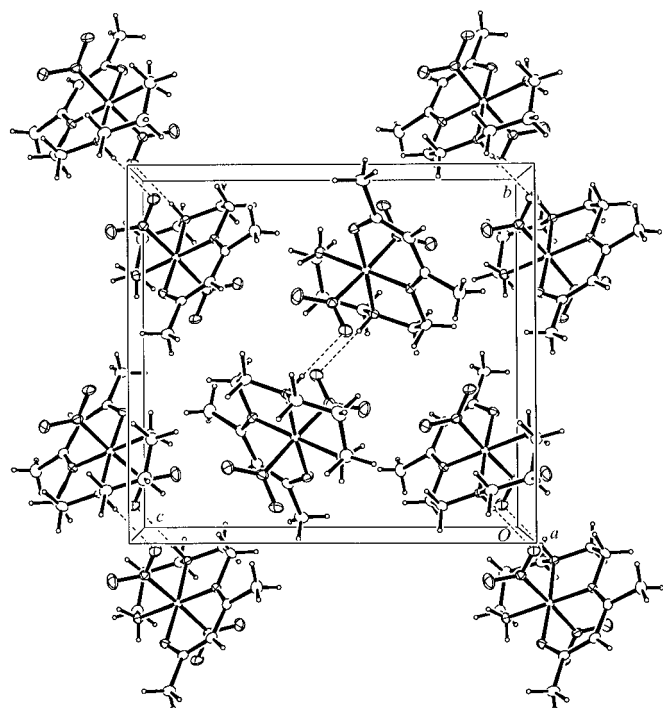


Figure 2  
ORTEP (Burnett & Johnson, 1996) view of (II) with displacement ellipsoids drawn at the 40% probability level.



**Figure 3**  
Packing diagram of (I), with the hydrogen bonding indicated.

bonding is found in other directions. The structure can therefore be described as a stack of one-dimensional strings along which the chirality of the molecules alternates. Also, the molecules of (I) are arranged such that the approximate planes of the tetradentate ligand are parallel to one another over the whole structure.



**Figure 4**  
Packing diagram of (II), with the hydrogen bonding indicated.

The packing diagram of (II) shows that there is only one intermolecular hydrogen bond, involving O4 and the H atom on N2 [ $d(\text{O} \cdots \text{H}) = 2.15(4) \text{ \AA}$ ]. The O atoms of the other nitro group have only very weak interactions with amine H atoms [ $d(\text{O} \cdots \text{H}) > 2.6 \text{ \AA}$ ]. As Fig. 4 clearly shows, the hydrogen bond is always formed by a pair of molecules around crystallographic inversion centers, and, unlike the other isomer, the planes of the tetradentate ligands are not parallel, but alternate along the  $c$  direction.

## Experimental

An aqueous solution (5 ml) containing  $\text{NaNO}_2$  (15 mmol) was added to an acetonitrile solution (25 ml) of  $\text{Co}(\text{acac})_3$  (5 mmol) (Bryan & Fernelius, 1957). The solution was mildly heated, and  $N$ -(2-aminoethyl)-1,3-propanediamine (10 mmol) was added. After further heating for 30 min, the solution was cooled to room temperature. A dark-brown residue obtained after the solution dried out (3 weeks) was washed with water (20 ml) (yield 45%). The crude product was dissolved in hot water, filtered through charcoal and recrystallized to give rod-shaped crystals of deep-red color, (I). The crystals were collected by filtration. Upon further standing, the filtrate gave dark-red brick-shaped crystals of larger size, (II). Analysis found (calculated) for the mixture: C 34.37 (34.39), H 5.77 (5.78), N 19.88% (20.06%).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 300 MHz, TMS):  $\delta$  (p.p.m.) = 176.97 (C=N), 166.24 (C=O), 96.11 (CH), 52.23, 51.00, 49.83, 39.60, 27.46 ( $5 \times \text{CH}_2$ ), 25.14, 22.44 ( $2 \times \text{CH}_3$ ).

## Compound (I)

### Crystal data

$[\text{Co}(\text{C}_{10}\text{H}_{20}\text{N}_3\text{O})(\text{NO}_2)_2]$   
 $M_r = 349.24$   
 Monoclinic,  $P2_1/c$   
 $a = 7.375(2) \text{ \AA}$   
 $b = 20.065(3) \text{ \AA}$   
 $c = 9.8088(9) \text{ \AA}$   
 $\beta = 91.717(7)^\circ$   
 $V = 1450.8(4) \text{ \AA}^3$   
 $Z = 4$

$D_x = 1.599 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 Cell parameters from 25 reflections  
 $\theta = 8.66\text{--}13.47^\circ$   
 $\mu = 1.213 \text{ mm}^{-1}$   
 $T = 293(2) \text{ K}$   
 Rod, dark red  
 $0.60 \times 0.17 \times 0.14 \text{ mm}$

### Data collection

Enraf-Nonius CAD-4 diffractometer  
 $\omega$ - $2\theta$  scans  
 Absorption correction:  $\psi$  scan  
 (NRCVAX ABSORP; Gabe *et al.*, 1989)  
 $T_{\min} = 0.776$ ,  $T_{\max} = 0.844$   
 2702 measured reflections  
 2554 independent reflections

1855 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.015$   
 $\theta_{\text{max}} = 24.96^\circ$   
 $h = -8 \rightarrow 8$   
 $k = 0 \rightarrow 23$   
 $l = 0 \rightarrow 11$   
 3 standard reflections  
 frequency: 240 min  
 intensity decay: none

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (I).

Co—O1	1.8886 (15)	Co—N4	1.977 (2)
Co—N1	1.903 (2)	N1—C4	1.298 (3)
Co—N5	1.937 (2)	O1—C2	1.289 (3)
Co—N2	1.962 (2)	C2—C3	1.367 (4)
Co—N3	1.971 (2)	C3—C4	1.416 (4)
O1—Co—N1	96.13 (8)	N5—Co—N4	178.19 (8)
O1—Co—N5	87.46 (7)	O1—C2—C3	125.7 (2)
O1—Co—N2	177.67 (7)	C2—C3—C4	126.1 (2)
N1—Co—N3	176.48 (8)	N1—C4—C3	122.9 (2)
N1—Co—N4	86.83 (8)		

**Table 2**  
Hydrogen-bonding geometry (Å, °) for (I).

<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>
N3—H2N...O5 <sup>i</sup>	0.83 (2)	2.45 (2)	3.209 (3)	129 (2)
N3—H3N...O2 <sup>ii</sup>	0.87 (2)	2.22 (2)	3.080 (3)	169 (2)

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

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.026$   
 $wR(F^2) = 0.064$   
 $S = 1.122$   
 2554 reflections  
 270 parameters

All H-atom parameters refined  
 $w = 1/[\sigma^2(F_o^2) + (0.0428P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = -0.004$   
 $\Delta\rho_{\max} = 0.25 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.36 \text{ e \AA}^{-3}$

**Compound (II)****Crystal data**

$[\text{Co}(\text{C}_{10}\text{H}_{20}\text{N}_3\text{O})(\text{NO}_2)_2]$   
 $M_r = 349.24$   
 Monoclinic,  $P2_1/c$   
 $a = 7.923 (3) \text{ \AA}$   
 $b = 13.1050 (10) \text{ \AA}$   
 $c = 14.0273 (13) \text{ \AA}$   
 $\beta = 91.908 (10)^\circ$   
 $V = 1455.7 (5) \text{ \AA}^3$   
 $Z = 4$

$D_x = 1.594 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 Cell parameters from 25 reflections  
 $\theta = 8.24\text{--}13.05^\circ$   
 $\mu = 1.208 \text{ mm}^{-1}$   
 $T = 293 (2) \text{ K}$   
 Brick, dark red  
 $0.52 \times 0.40 \times 0.30 \text{ mm}$

**Data collection**

Enraf–Nonius CAD-4 diffractometer  
 $\omega$ - $2\theta$  scans  
 Absorption correction:  $\psi$  scan  
 (NRCVAX ABSORP; Gabe *et al.*, 1989)  
 $T_{\min} = 0.648$ ,  $T_{\max} = 0.696$   
 2672 measured reflections  
 2568 independent reflections

1985 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.039$   
 $\theta_{\max} = 24.99^\circ$   
 $h = -9 \rightarrow 9$   
 $k = 0 \rightarrow 15$   
 $l = 0 \rightarrow 16$   
 3 standard reflections  
 frequency: 240 min  
 intensity decay: none

**Refinement**

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.032$   
 $wR(F^2) = 0.105$   
 $S = 1.266$   
 2568 reflections  
 270 parameters  
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0464P)^2 + 2.1606P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = -0.002$   
 $\Delta\rho_{\max} = 0.37 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.48 \text{ e \AA}^{-3}$

For both 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

**Table 3**  
Selected geometric parameters (Å, °) for (II).

Co—O1	1.880 (3)	Co—N3	1.968 (3)
Co—N1	1.901 (3)	N1—C4	1.294 (5)
Co—N4	1.953 (3)	O1—C2	1.293 (4)
Co—N2	1.956 (3)	C2—C3	1.362 (6)
Co—N5	1.965 (3)	C3—C4	1.423 (6)
O1—Co—N1	96.35 (12)	N1—Co—N3	179.06 (14)
N1—Co—N4	91.19 (13)	O1—C2—C3	126.1 (3)
O1—Co—N2	176.28 (13)	C2—C3—C4	126.1 (4)
O1—Co—N5	88.30 (13)	N1—C4—C3	122.6 (3)
N4—Co—N5	176.66 (13)		

**Table 4**  
Hydrogen-bonding geometry (Å, °) for (II).

<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>
N2—H1N...O4 <sup>i</sup>	0.84 (4)	2.15 (4)	2.966 (4)	164 (4)

Symmetry code: (i)  $-x, -y, -z$ .

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: DA1150). Services for accessing these data are described at the back of the journal.

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