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On the Crystal Structures of *cis*- and *trans*-Bis(ethylenediamine)-dinitrocobalt(III) Nitrate

OLLE BÖRTIN

Department of Inorganic Chemistry, University of Göteborg and Chalmers University of Technology, P.O. Box, S-402 20 Göteborg 5, Sweden

The crystal structure of *trans*-bis(ethylenediamine)dinitrocobalt(III) nitrate has been refined. The crystals are monoclinic with $a=13.819(5)$ Å, $b=9.680(2)$ Å, $c=9.095(2)$ Å, $\beta=105.83(2)°$, $V=1170.4$ Å^3, $Z=4$ and space group $P2_1/a$. Least-squares refinement of the structure, based on 4212 reflections, gave an R-value of 0.05. The *trans*-bis(ethylenediamine)-dinitrocobalt(III) ions are arranged in a cubic close-packed manner with the nitrate ions in the octahedral holes. The cobalt atom is octahedrally coordinated by six nitrogen atoms with the bond distances: Co—N (to NO_2) 1.937—1.939(2) Å, and Co—N (to en) 1.942—1.959(2) Å.

In connection with studies of nitro and nitrito compounds of transition metals the crystal structures of pentaamminenitrocobalt(III) chloride [1] and *cis*- and *trans*-bis(ethylenediamine)-dinitrocobalt(III) nitrate [2,3] were determined. Some of the bond distances in *trans*-$[Co(NO_2)_2(en)_2]NO_3$ were surprising, *e.g.* Co—N (to NO_2) 1.81 and 2.02 Å. There were also large differences between the N—O bonds in the nitro groups and in the nitrate ions. In order to ascertain whether or not these differences in bond distances were correct a new refinement of the structure has been performed.

trans-$[Co(NO_2)_2(en)_2]NO_3$

Crystal data. $a=13.819(5)$ Å, $b=9.680(2)$ Å, $c=9.095(2)$ Å, $\beta=105.83(2)°$, $V=1170.4$ Å^3, $Z=4$, space group $P2_1/a$, $D_c=1.92$ g cm^{-3}.

Refinement. The refinement was based on the $0kl-26kl$ intensities recorded with a Philips Pailred automatic single crystal diffractometer with Mo$K\alpha$ radiation, monochromatized with a graphite crystal. All intensities were corrected for Lorentz and polarization effects using the program DATAP1. The atomic scattering factors used for Co, N, O, and C were those calculated by Doyle and Turner.[4] The structure factors were weighted according to Cruickshank [5] with $a=30.0$ and $c=0.01$. The scale-factors of the separate layers were refined. It was noticed that, when the scale-factors were plotted against the layer number, those of the even layers yielded a smooth curve while those of the odd layers did not. The scale-factors of the odd layers were assigned values corresponding to this curve and refinement based only on the odd layers was undertaken, an overall scale-factor being refined. This caused the x-coordinate of the cobalt atom to change from 0.1205 to 0.1295, corresponding to a displacement of 0.12 Å. The refinement was continued with anisotropic thermal parameters with the complete three-dimensional data. At this stage a difference syntheses was performed giving the positions of the hydrogen atoms. The electron densities corresponding to the hydrogen atoms varied between 0.6 and 1.1 e Å^{-3}, while the highest spurious peak, which was situated at the position of the cobalt atom, had a height of 1.0 e Å^{-3}. The coordinates and isotropic temperature factors of the hydrogen atoms were refined using the scattering factors for hydrogen calculated by Stewart.[6] Finally separate scale-factors were refined for each layer and the reliability index converged to 0.05. The resulting parameters for the heavier atoms are given in Table 1 and for the hydrogen atoms in Table

Table 1. Final atomic parameters for *trans*-$[Co(NO_2)_2(en)_2]NO_3$ (standard deviations in parentheses). The anisotropic temperature factor is $\exp\{-(h^2(a^*)^2u_{11}+k^2(b^*)^2u_{22}+l^2(c^*)^2u_{33}+2hka^*b^*u_{12}+2hla^*c^*u_{13}+2klb^*c^*u_{23})\}$.

Atom	x	y	z	$u_{ij}\times 10^4$ u_{11}	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}
Co	0.12934(2)	0.25934(3)	0.25261(4)	128(1)	131(1)	137(1)	−1(1)	20(1)	5(1)
N1	0.2719(2)	0.3494(3)	0.3515(3)	178(6)	269(9)	211(8)	−18(8)	21(7)	16(8)
O11	0.3094(2)	0.1238(3)	0.3772(4)	244(9)	379(12)	550(17)	85(9)	−34(11)	112(12)
O12	0.3258(2)	0.3431(3)	0.3864(3)	235(8)	397(12)	463(15)	−107(9)	−1(10)	−48(11)
N2	−0.0126(2)	0.2834(3)	0.1532(3)	177(7)	270(9)	211(9)	49(7)	21(7)	16(8)
O21	−0.0473(2)	0.4000(3)	0.1279(3)	296(10)	334(11)	512(16)	116(10)	−4(11)	80(11)
O22	−0.0675(2)	0.1811(3)	0.1182(3)	193(8)	381(12)	485(15)	−51(9)	−23(9)	−39(11)
N31	0.0969(2)	0.1202(2)	0.3858(3)	248(8)	190(8)	206(9)	−35(7)	35(8)	14(7)
C32	0.1045(2)	0.1805(4)	0.5389(3)	328(11)	356(14)	171(10)	−34(11)	71(10)	35(10)
C33	0.0683(2)	0.3281(4)	0.5143(4)	258(10)	332(13)	272(13)	−19(10)	92(11)	−54(11)
N34	0.1201(2)	0.3919(2)	0.4086(3)	266(8)	213(8)	232(10)	−25(8)	74(9)	−25(8)
N41	0.1381(2)	0.1229(2)	0.0977(3)	184(7)	204(8)	211(9)	2(7)	26(7)	−22(7)
C42	0.1917(2)	0.1840(3)	−0.0058(3)	229(8)	330(13)	231(11)	29(9)	104(10)	−11(10)
C43	0.1569(2)	0.3327(3)	−0.0341(4)	281(10)	312(13)	230(11)	−14(10)	80(10)	32(10)
N44	0.1627(2)	0.3963(2)	0.1170(3)	258(9)	205(8)	223(10)	−31(8)	35(9)	35(7)
N5	0.3838(2)	0.2912(3)	0.7556(3)	385(11)	234(8)	243(9)	18(9)	112(10)	4(9)
O51	0.3807(3)	0.1636(3)	0.7515(4)	970(26)	217(9)	573(19)	46(15)	171(20)	−3(12)
O52	0.4660(2)	0.3545(3)	0.7906(3)	276(10)	531(15)	440(15)	5(11)	42(11)	119(13)
O53	0.3040(2)	0.3609(3)	0.7233(4)	284(10)	385(12)	499(15)	18(10)	38(11)	−97(12)

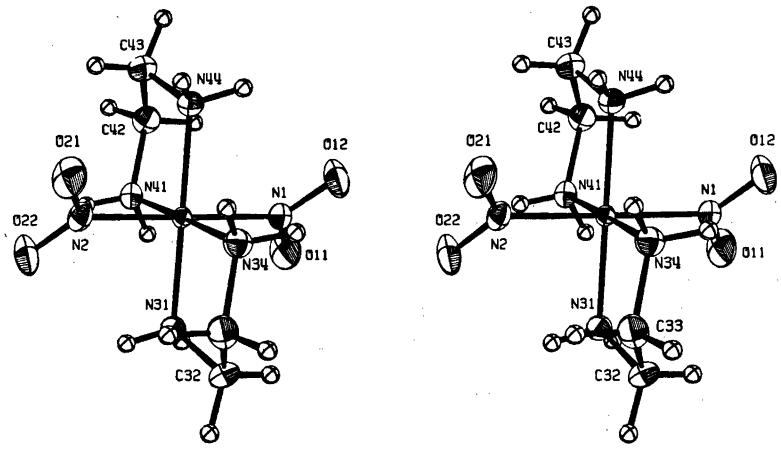

Fig. 1. A stereoscopic view of the ion *trans*-$[Co(NO_2)_2(en)_2]^+$.

2. A list of observed and calculated structure factors can be obtained from the author on request. The *trans*-$[Co(NO_2)_2(en)_2]^+$ ion is shown in Fig. 1, and the unit cell in Fig. 2, drawn with ORTEP. Bond distances and some angles are given in Table 3, together with their standard deviations. Distances and angles for hydrogen bonds are given in Table 4.

cis-$[Co(NO_2)_2(en)_2]NO_3$

Crystal data. $a=11.745(2)$ Å, $b=16.090(3)$ Å, $c=6.512(1)$ Å, $\beta=98.92(2)°$, $V=1215.8$ Å^3 $Z=4$, space group $P2_1/n$, $D_c=1.82$ g cm^{-3}, $D_o=1.85$ g cm^{-3}.

A brief account of the crystal structure analysis of this compound has been published.[2] The *cis*-bis(ethylenediamine)dinitrocobalt(III) ion is shown in Fig. 3 and some bond distances and angles are given in Table 5.

Table 2. Final parameters of hydrogen atoms. The temperature factor is $\exp(-B \sin^2\theta/\lambda)$.

Atom	x	y	z	B
H311	0.037(4)	0.091(5)	0.349(5)	3.7(11)
H312	0.132(3)	0.042(4)	0.391(5)	2.4(8)
H321	0.067(4)	0.128(5)	0.602(5)	3.6(10)
H322	0.167(3)	0.174(5)	0.588(5)	3.2(10)
H331	−0.005(3)	0.336(4)	0.464(4)	1.9(8)
H332	0.082(4)	0.389(5)	0.607(6)	4.2(11)
H341	0.093(3)	0.472(4)	0.371(5)	2.8(9)
H342	0.184(4)	0.426(6)	0.464(6)	5.2(13)
H411	0.078(3)	0.100(4)	0.053(4)	2.2(8)
H412	0.168(3)	0.038(4)	0.152(5)	2.8(9)
H421	0.176(3)	0.122(5)	−0.105(5)	3.4(10)
H422	0.264(3)	0.172(5)	0.049(5)	3.0(10)
H431	0.090(3)	0.344(4)	−0.083(5)	2.4(8)
H432	0.199(3)	0.387(5)	−0.081(5)	2.8(9)
H441	0.129(3)	0.474(5)	0.107(5)	2.9(9)
H442	0.224(3)	0.438(5)	0.164(5)	3.0(9)

Table 3. Bond distances and angles in *trans*-$[Co(NO_2)_2(en)_2]NO_3$ (standard deviations in parentheses). Angles round Co not indicated in the table are 88.6–91.2° or 178.8–179.0°. Bond distances N–H are 0.84–0.99(5) Å, mean 0.90 Å, and C–H 0.86–1.06(5) Å, mean 0.98 Å.

Distance (Å)		Angle (°)	
Co –N1	1.939(2)	N31–Co –N34	86.0(1)
Co –N2	1.937(2)	N31–Co –N41	92.9(1)
Co –N31	1.944(2)	N34–Co –N44	95.0(1)
Co –N34	1.942(3)	N41–Co –N44	86.1(1)
Co –N41	1.959(2)	Co –N1 –O11	120.1(2)
Co –N44	1.950(2)	Co –N1 –O12	120.2(2)
N1 –O11	1.228(4)	O11–N1 –O12	119.8(2)
N1 –O12	1.238(4)	Co –N2 –O21	119.6(2)
N2 –O21	1.224(4)	Co –N2 –O22	119.8(2)
N2 –O22	1.236(4)	O21–N2 –O22	120.6(2)
N31–C32	1.487(4)	Co –N31–C32	110.0(2)
C32–C33	1.509(5)	N31–C32–C33	107.3(2)
C33–N34	1.482(4)	C32–C33–N34	106.9(2)
N41–C42	1.471(4)	C33–N34–Co	109.8(2)
C42–C43	1.517(5)	Co –N41–C42	109.3(2)
C43–N44	1.487(4)	N41–C42–C43	107.3(2)
		C42–C43–N44	107.5(2)
N5 –O51	1.235(4)	C43–N44–Co	109.9(2)
N5 –O52	1.253(4)		
N5 –O53	1.258(4)	O51–N5 –O52	121.2(3)
		O51–N5 –O53	120.6(3)
		O52–N5 –O53	118.2(3)

DESCRIPTION AND DISCUSSION

The cobalt atoms of *cis*- and *trans*-$[Co(NO_2)_2(en)_2]^+$ ions are octahedrally coordinated by the nitrogen atoms from two nitro groups and two ethylenediamine groups. The greater *trans* effect of the nitro group is obvious. The bond distances Co–N (to NO_2) are 1.937–1.939(2) Å in the *trans* compound and 1.887–1.918(17) Å when the nitro groups are in *trans* position to amine nitrogen atoms in the *cis* compound. The bond distances Co–N (to en) are 1.991–1.997(17) Å when *trans* to NO_2 in the *cis* compound, and 1.942–1.959(2) Å and 1.941–1.971(17) Å when *trans* to an other amine nitrogen atom in the *trans* respectively *cis* compounds.

Table 4. Hydrogen bonds N–H···O in *trans*-$[Co(NO_2)_2(en)_2]NO_3$.

Atoms N	H	O	Distances (Å) H–O	N–O	Angle (°) N–H–O
N31	H311	O22	2.36	2.90	121 [a]
N31	H312	O53	2.33	3.15	152
N34	H341	O51	2.24	3.01	143
N34	H342	O11	2.39	2.96	118
N34	H342	O12	2.39	2.94	117 [a]
N41	H411	O22	2.38	2.95	125 [a]
N41	H412	O53	2.03	3.00	166
N44	H441	O21	2.45	3.08	128
N44	H441	O51	2.27	2.98	139
N44	H442	O12	2.32	2.89	119 [a]

[a] All atoms belong to the same complex ion.

Table 5. Bond distances and angles in the *cis*-bis-(ethylenediamine)dinitrocobalt(III) ion (standard deviations in parentheses). Angles round Co not indicated in the table are 88.8–92.5° or 175.7–176.8°.

Distance (Å)		Angle (°)	
Co –N1	1.887(17)	N31–Co –N34	85.9(7)
Co –N2	1.918(18)	N41–Co –N44	85.1(7)
Co –N31	1.941(17)	Co –N1 –O11	122.6(14)
Co –N34	1.997(14)	Co –N1 –O12	121.3(13)
Co –N41	1.971(16)	O11–N1 –O12	116.1(17)
Co –N44	1.991(17)	Co –N2 –O21	121.4(14)
N1 –O11	1.229(22)	Co –N2 –O22	119.5(14)
N1 –O12	1.231(22)	O21–N2 –O22	118.7(18)
N2 –O21	1.211(26)	Co –N31–C32	111.4(13)
N2 –O22	1.226(26)	N31–C32–C33	109.9(19)
N31–C32	1.501(28)	C32–C33–N34	108.2(18)
C32–C33	1.470(34)	C33–N34–Co	108.3(11)
C33–N34	1.528(25)	Co –N41–C42	113.4(13)
N41–C42	1.469(27)	N41–C42–C43	105.9(16)
C42–C43	1.564(31)	C42–C43–N44	109.6(17)
C43–N44	1.505(26)	C43–N44–Co	108.9(12)

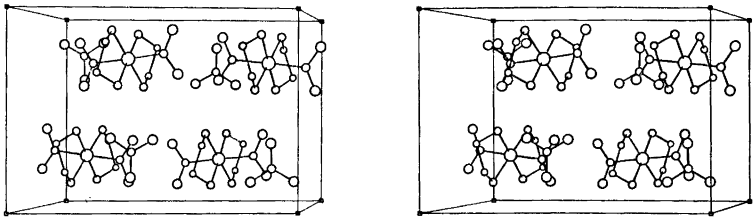

Fig. 2. A stereoscopic view of the structure of *trans*-bis(ethylenediamine)dinitrocobalt(III) nitrate.

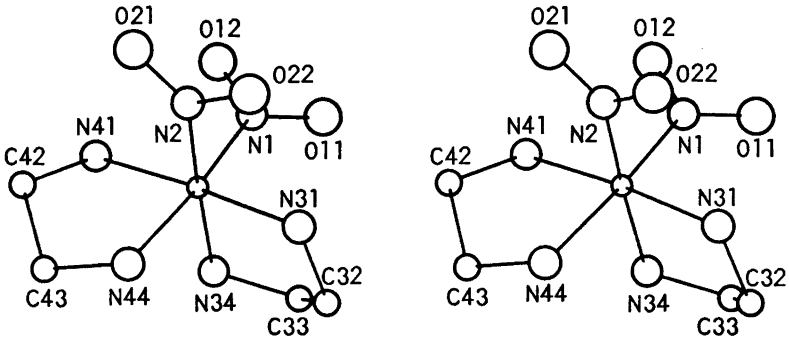

Fig. 3. A stereoscopic view of the ion *cis*-$[Co(NO_2)_2(en)_2]^+$.

When a plane is drawn through the cobalt atom and the nitrogen atoms of an ethylenediamine group, the carbon atoms will be situated on either side of it and at different distances, 0.18 and 0.41 Å for one group and 0.28 and 0.34 Å for the other for the *cis* compound and 0.26 and 0.40 Å for one group and 0.29 and 0.37 Å for the other for the *trans* compound.

The large complex ions are arranged in close-packed manners. In *trans*-bis(ethylenediamine)-dinitrocobalt(III) nitrate the cations are ordered in a cubic close-packed manner and, as the nitrate ions occupy the octahedral holes, the structure can be visualised as a distorted sodium chloride structure. In *cis*-bis(ethylenediamine)dinitrocobalt(III) nitrate the nitrate ions occupy tetrahedral holes between the cations with two nitrate ions fairly close to one another with a separation of 3.23 Å between the nitrogen atoms. The complex ions are linked to one another and to the nitrate ions by means of hydrogen bonds N–H···O. The shortest N–O distance indicating this in the *cis* compound is 2.89 Å. In the *trans* compound there are also hydrogen bonds N–H···O within the complex ions.

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