The Crystal Structure of two Conformational Isomers of

meridional-Trinitro(ammine)ethylenediaminecobalt(III),

[Co(NO₂)₃NH₃en]

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The coordination compound [Co(NO₂)₃NH₃en] exists in two forms having different crystal habits and colours, (brown and yellow). Both forms crystallize in the space group $P2_1/c$ with 4 formula units per unit cell. The cell constants are:

$a = 10.50$ Å, $b = 6.65$ Å, $c = 13.81$ Å, $\beta = 103.1°$ (brown form).
$a = 9.58$ Å, $b = 8.37$ Å, $c = 11.77$ Å, $\beta = 92.9°$ (yellow form).

Complete X-ray structure analyses of the two forms were based on three-dimensional intensity data collected by means of an automated Weissenberg diffractometer. The structures were solved and refined by application of conventional Fourier and least squares calculations. The final R values are 0.058 (brown form) and 0.066 (yellow form). The structures are very similar. The coordination polyhedron around the Co atom is a slightly distorted octahedron in both cases. In both compounds the three nitro groups are in the 1,2,6 positions, *i.e.* both are *meridional* forms. The essential difference is the *conformations* of the nitro groups. Either structure may be transformed into the other by rotating the nitro groups around their respective Co—N bonds. The two forms of [Co(NO₂)₃NH₃en] are therefore termed *rotational* or *conformational* isomers (conformers). As far as the authors are aware, this is the first observation of this type of isomerism in coordination compounds.

This paper reports three-dimensional crystal structure analyses of the two different forms of the compound [Co(NO₂)₃NH₃en]. The preparation and general properties of the compounds are the subject matter of a following paper by MacDermott and Barfoed.[1] The X-ray crystallographic investigation was suggested by the said authors, who kindly placed suitable single crystals at our disposal.

DESCRIPTION OF THE CRYSTALS

[Co(NO$_2$)$_3$NH$_3$en] crystallizes in two forms, termed "brown" and "yellow", having quite different habits. The brown crystals form octahedra. The faces {100}, {001} and {$\bar{1}$11} are equally developed. The yellow crystals are needle-shaped, [010] is the needle axis. The faces {100} and {001} are well developed, while the faces {111} and {$\bar{1}$11} show up in a few cases only.

Both forms crystallize in the space group $P2_1/c$, which is unequivocally determined by the systematic extinctions; $h0l$ absent for l odd, and $0k0$ absent for k odd.

The unit cell constants derived from precession photographs (Mo$K\alpha$, $\lambda = 0.71069$ Å) are; brown form: $a = 10.50$ Å, $b = 6.65$ Å, $c = 13.81$ Å, $\beta = 103.1°$; yellow form: $a = 9.58$ Å, $b = 8.37$ Å, $c = 11.77$ Å, $\beta = 92.9°$. The relative standard deviation of the linear constants estimated from repeated measurements is 0.2 %. The estimated standard deviation of the angular measurements is 0.1°. The cell volumes are virtually equal, being 939 Å^3 for the brown form and 943 Å^3 for the yellow form. The observed density (flotation) is 1.93 g·cm^{-3} for both compounds $i.e.$ $Z = 4.0$.

COLLECTION OF INTENSITY DATA

Intensity data were collected by means of an automatic Weissenberg diffractometer, delivered by STOE & CIE GMBH, Hilpertstrasse 10, Darmstadt, DBR. Mo$K\alpha$ radiation was selected using a LiF monochromator. Harmonics were excluded by using a scintillation detector with proper settings of a pulse height discriminator.

Brown form. A nearly isodiametric (0.40 mm) crystal was mounted with the b-axis as rotation axis. All the non-extinct reflexions $h0l$ through $h7l$ were measured using ω-scan. The constancy of the primary beam and the counting system was checked by frequent remeasurements of a standard reflexion. Net intensities less than twice the standard deviation were rejected as non-observable, leaving a total of 1791 independent observations for the subsequent analysis.

Yellow form. A needle-shaped crystal of dimensions 0.11 × 0.25 × 0.11 mm was used with the needle axis (b-axis) as rotation axis. The ω-scan of the reflexions $h0l$ through $h8l$ yielded 1438 independent observations.

In neither case corrections for absorption were applied, ($\mu_{Mo} = 18$ cm^{-1}).

Computer programs. The FORTRAN program PAULUS 67, supplied by the manufacturer of the diffractometer, calculates the setting angles, ω and Υ, from the cell data. The ALGOL program PDR controls the internal consistency of the diffractometer output and calculates the net reflected intensity and the standard deviation (based on counting statistics). The FORTRAN program LP converts the net intensities to relative structure factors by means of the conventional Lp correction formulas, ignoring the partial polarization of the primary beam. The system of X-RAY 63 crystallographic programs edited by J. Stewart, the University of Maryland, performs the several calculations needed for the regular structural analysis.

The calculations were made on the IBM 7090/94 computer at NEUCC and on the GIER computer, both situated at the Technical University of Denmark.

STRUCTURE ANALYSIS

Brown form. The cobalt atom was located from a three-dimensional Patterson map by means of the Harker section $P(x\frac{1}{2}z)$ and the Harker line $P(0y\frac{1}{2})$. The positions of the remaining non-hydrogen atoms were determined by means of a series of Fourier syntheses. Atomic scattering factors were taken from Volume III of *International Tables of Crystallography*, 1962. The parameters obtained so far were refined by a full-matrix least squares procedure applying the weights $w=1/\sigma(F_0{}^2)$. This initial refinement with isotropic thermal parameters included all observed structure factors and terminated with R equal to 0.11 (weighted $R=0.12$) In order to eliminate the influence from the hydrogen atoms 290 reflexions having $\sin\theta/\lambda < 0.35$ were omitted from the next step of refinement, where anisotropic thermal parameters were introduced. This lowered the R value to 0.076 (weighted $R=0.106$). No further refinement was obtained by introduction of interlayer scale factors.

The positions of the hydrogen atoms were revealed from three-dimensional difference-Fourier syntheses including either all observed structure factors

Table 1a. Brown form. Atomic coordinates and standard deviations.

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
Co	0.2770	(1)	0.0423	(1)	0.3079	(1)
N1	0.1061	(5)	0.0145	(7)	0.3377	(4)
N2	0.3007	(5)	0.2769	(7)	0.3917	(4)
N3	0.3513	(5)	−0.1333	(7)	0.4185	(4)
N4	0.2455	(4)	−0.1916	(7)	0.2178	(4)
N5	0.2023	(5)	0.1986	(7)	0.1896	(4)
N6	0.4513	(5)	0.0812	(7)	0.2850	(4)
O11	0.0188	(6)	0.1286	(11)	0.3057	(6)
O12	0.0833	(6)	−0.1214	(11)	0.3492	(5)
O21	0.2622	(7)	0.4399	(7)	0.3569	(4)
O22	0.3473	(7)	0.2676	(8)	0.4798	(4)
C4	0.2106	(7)	−0.1254	(10)	0.1135	(5)
C5	0.1297	(7)	0.0614	(10)	0.1091	(5)
O61	0.4686	(5)	0.1258	(9)	0.2028	(4)
O62	0.5488	(4)	0.0679	(8)	0.3530	(4)
H31	0.3474	(80)	−0.0691	(118)	0.4723	(61)
H32	0.4280	(81)	−0.1790	(117)	0.4120	(60)
H33	0.3029	(81)	−0.2283	(120)	0.4262	(59)
H41	0.1825	(78)	−0.2746	(113)	0.2304	(57)
H42	0.3207	(80)	−0.2862	(117)	0.2322	(58)
H51	0.1442	(79)	0.2961	(114)	0.1963	(59)
H52	0.2747	(77)	0.2642	(115)	0.1605	(58)
H43	0.1638	(79)	−0.2378	(116)	0.0679	(58)
H44	0.2985	(78)	−0.1150	(115)	0.0894	(58)
H53	0.0457	(81)	0.0279	(109)	0.1250	(61)
H54	0.1327	(77)	0.1234	(116)	0.0366	(60)

or only those having $\sin\theta/\lambda < 0.35$. A few reflexions having a large value of ΔF were omitted from this part of the analyses. All the hydrogen atoms appeared at tetrahedral positions around the nitrogen and the carbon atoms.

Next, the least squares refinement was reassumed. The thermal movements of the hydrogen atoms were approximately accounted for by a fixed isotropic B parameter equal to 3.0. All the observed structure factors except three rather discrepant structure factors were included in this final refinement, which proceeded in three stages, each consisting of two cycles: The anisotropic thermal parameters and the positional parameters of all non-hydrogen atoms were refined in the first and second stage, respectively. The positional parameters of the hydrogen atoms were refined in the third stage. The final R value was 0.058 (weighted $R=0.072$).

Yellow form. The analysis of data for the yellow crystal proceeded along the same line. The final R value was 0.066 (weighted $R=0.077$).

A list of observed and calculated structure factors may be obtained from the authors. Atomic coordinates in fractions of the unit cell, and the thermal parameters are listed in Tables 1a and 2a (brown form) and in Tables 1b and 2b (yellow form).

Table 1b. Yellow form. Atomic coordinates and standard deviations.

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
Co	0.2431	(1)	−0.0468	(1)	0.1943	(1)
N1	0.0421	(7)	−0.0496	(8)	0.1658	(6)
N2	0.2266	(8)	−0.1190	(8)	0.3485	(6)
N3	0.2528	(7)	−0.2676	(7)	0.1440	(6)
N4	0.2690	(6)	0.0361	(8)	0.0410	(5)
N5	0.2311	(7)	0.1749	(7)	0.2407	(6)
N6	0.4433	(7)	−0.0409	(8)	0.2214	(6)
O11	−0.0350	(7)	0.0426	(9)	0.2138	(7)
O12	−0.0118	(6)	−0.1423	(8)	0.0962	(6)
O21	0.1628	(9)	−0.0378	(9)	0.4152	(6)
O22	0.2870	(8)	−0.2434	(7)	0.3807	(6)
C4	0.3088	(10)	0.2084	(9)	0.0495	(8)
C5	0.2166	(10)	0.2808	(9)	0.1371	(7)
O61	0.4946	(7)	0.0222	(8)	0.3085	(6)
O62	0.5206	(7)	−0.1033	(8)	0.1514	(6)
H31	0.1777	(115)	−0.3483	(122)	0.1696	(91)
H32	0.3438	(116)	−0.3187	(124)	0.1537	(93)
H33	0.2387	(120)	−0.2833	(118)	0.0736	(95)
H41	0.1855	(113)	0.0356	(118)	−0.0115	(89)
H42	0.3405	(114)	−0.0138	(114)	−0.0005	(90)
H51	0.1570	(117)	0.1676	(121)	0.2900	(90)
H52	0.3224	(116)	0.1802	(124)	0.2805	(90)
H43	0.2964	(116)	0.2811	(116)	−0.0206	(91)
H44	0.4254	(114)	0.2065	(119)	0.0832	(89)
H53	0.1141	(112)	0.2858	(116)	0.1024	(89)
H54	0.2349	(110)	0.4090	(120)	0.1672	(87)

Table 2a. Brown form. Thermal parameters as they appear in the expression.
$\exp-1/4(h^2a^{*2}B_{11}+k^2b^{*2}B_{22}+l^2c^{*2}B_{33}+2hka^*b^*B_{12}+2hla^*c^*B_{13}+2klb^*c^*B_{23})$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	1.05	1.58	1.31	−0.03	0.19	−0.04
N1	1.76	2.56	2.78	−0.18	0.49	−0.07
N2	2.46	2.40	2.62	0.19	0.19	−0.43
N3	2.03	2.54	2.31	−0.00	0.33	0.03
N4	1.73	1.91	2.04	−0.20	0.37	−0.74
N5	2.38	2.63	1.78	0.38	−0.04	0.28
N6	1.53	2.21	2.25	−0.18	0.26	0.11
O11	3.44	9.71	10.39	3.63	3.42	5.25
O12	3.23	8.97	8.46	−0.30	2.29	4.48
O21	9.05	2.47	3.97	0.30	−0.20	0.00
O22	8.27	4.92	3.19	2.38	−1.90	−1.87
C4	2.98	4.19	2.14	0.54	0.18	−0.77
C5	2.84	3.89	2.23	0.55	−0.28	−0.12
O61	2.24	7.95	2.83	−1.09	0.83	1.60
O62	1.66	6.38	3.45	−1.04	−0.41	1.32

Table 2b. Yellow form. Thermal parameters as they appear in the expression.
$\exp-1/4(h^2a^{*2}B_{11}+k^2b^{*2}B_{22}+l^2c^{*2}B_{33}+2hka^*b^*B_{12}+2hla^*c^*B_{13}+2klb^*c^*B_{23})$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	1.16	1.54	0.94	0.03	−0.05	0.02
N1	2.11	2.42	2.64	−0.43	−0.29	0.25
N2	3.23	2.95	2.09	−0.23	0.19	0.20
N3	2.90	1.07	2.79	−0.24	−0.10	−0.36
N4	1.72	2.60	1.85	−0.55	0.17	−0.28
N5	2.27	2.28	1.60	0.25	0.17	−0.56
N6	1.89	2.28	2.84	−0.36	−0.25	0.50
O11	1.80	6.03	6.47	0.23	0.95	−1.85
O12	2.17	4.36	4.83	−0.54	−1.14	−0.69
O21	7.16	4.85	2.65	0.65	2.19	−0.18
O22	6.17	3.54	2.98	0.72	−0.69	1.74
C4	2.54	2.51	2.80	−0.01	0.34	0.14
C5	3.55	1.61	2.35	0.52	−0.08	0.42
O61	2.74	5.68	4.25	−0.54	−1.54	−0.04
O62	1.81	4.61	4.42	0.82	0.73	0.07

DISCUSSION

The structure of the two forms of the $[Co(NO_2)_3NH_3en]$ complex is shown in Fig. 1a and b. The three nitro groups are in the 1,2,6 positions in both cases, *i.e.* both are *meridional* forms. The essential difference is due to the *conformations* of the nitro groups, *i.e.* either form may be transformed into the other by rotating the nitro groups around their respective Co—N bonds. The two forms of $[Co(NO_2)_3NH_3en]$ are therefore termed *rotational* or *conformational* isomers (conformers). As far as the authors are aware, this is the first observation of this type of isomerism in coordination compounds.

The details of the conformations are illustrated in Fig. 2a and b. In the yellow isomer the plane determined by the nitro group (6) nearly bisects the angle N5—Co—N2. If the nitro group is turned 68° anticlockwise around its
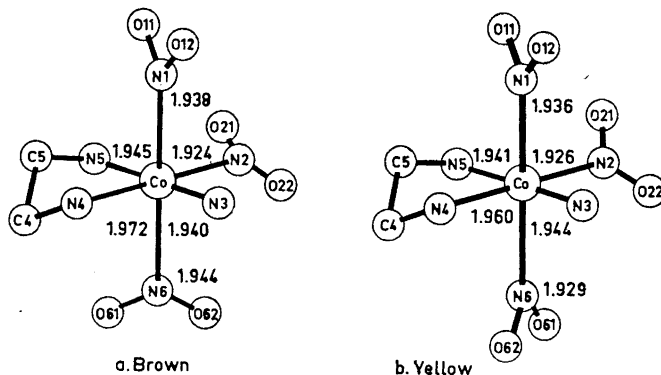
Fig. 1. Perspective drawings of the two forms of [Co(NO₂)₃NH₃en].

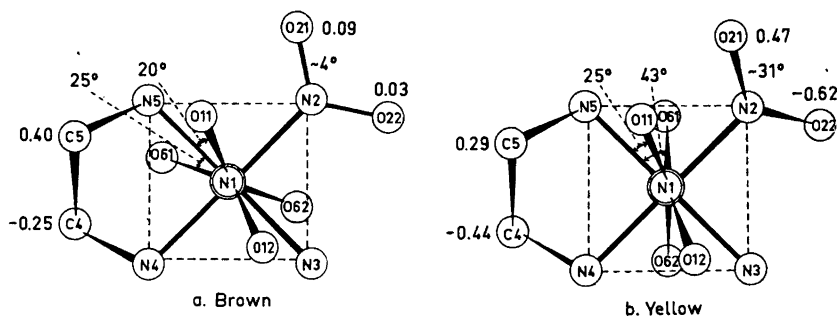*Fig. 2.* The two forms of [Co(NO₂)₃NH₃en] viewed perpendicularly to the least squares plane through N2, N3, N4, N5. Some distances (in Å) from this plane and also the angle of the nitro group (2) with the same plane are given. The twists of the nitro groups (1) and (6) (*cf.* Fig. 1) with respect to the least squares plane through N1, N3, N6, N5 are also shown.

Co—N bond the conformation of the nitro group (6) in the brown isomer is obtained. The concurrent shift of C5 from 0.29 to 0.40 Å above the best plane through N2, N3, N4, N5 (Table 5) is ascribed to the space requirement of O61. A space filling model of the complex shows that these two conformations of nitro group (6) are the only reasonable ones. A free shift from one conformation to the other is hindered by the nitrogen atom N5 and the hydrogen atom H52 (Table 6).

The nitro groups (1) and (2) also show two different conformations (Fig. 2). As for the latter the angle between that group and the best plane through N2, N3, N4, N5 is 4° in the brown form and 31° in the yellow form. In either case the oxygen atoms O21 and O22 are pushed as far away as possible from the oxygen atoms of the other nitro groups. The angular difference between the two conformations of nitro group (1) is only 5°.

Table 3. Interatomic distances and standard deviations.

a. Brown form.			b. Yellow form.		
Atoms	Distances	(Å)	Atoms	Distances	(Å)
Co —N1	1.938	(7)	Co —N1	1.936	(7)
Co —N2	1.924	(6)	Co —N2	1.926	(8)
Co —N3	1.940	(5)	Co —N3	1.944	(7)
Co —N4	1.972	(5)	Co —N4	1.960	(7)
Co —N5	1.945	(6)	Co —N5	1.941	(7)
Co —N6	1.944	(6)	Co —N6	1.929	(8)
N1—O11	1.194	(8)	N1—O11	1.226	(10)
N1—O12	1.207	(9)	N1—O12	1.224	(10)
N2—O21	1.217	(7)	N2—O21	1.226	(11)
N2—O22	1.206	(8)	N2—O22	1.241	(10)
N4—C4	1.471	(8)	N4—C4	1.494	(11)
N5—C5	1.505	(8)	N5—C5	1.508	(10)
N6—O61	1.226	(8)	N6—O61	1.232	(10)
N6—O62	1.224	(6)	N6—O62	1.250	(10)
C4 —C5	1.497	(10)	C4 —C5	1.518	(13)
N3—H31	0.866	(85)	N3—H31	1.042	(108)
N3—H32	0.884	(88)	N3—H32	0.973	(110)
N3—H33	0.833	(84)	N3—H33	0.843	(111)
N4—H41	0.908	(83)	N4—H41	0.986	(105)
N4—H42	0.993	(80)	N4—H42	0.958	(108)
N5—H51	0.908	(81)	N5—H51	0.941	(112)
N5—H52	1.034	(87)	N5—H52	0.972	(108)
C4 —H43	1.028	(75)	C4 —H43	1.027	(104)
C4 —H44	1.052	(88)	C4 —H44	1.167	(108)
C5 —H53	0.982	(89)	C5 —H53	1.044	(106)
C5 —H54	1.089	(84)	C5 —H54	1.141	(101)

The bond lengths in the two structures are nearly identical (Table 3, a and b). The Co—N (nitro) bond lengths (Fig. 1) are found in the range 1.924 Å to 1.944 Å (e.s.d. 0.007 Å) having an average value of 1.933 Å. The other Co—N bond lengths range from 1.940 Å to 1.972 Å (average value 1.950 Å). This disparity, though small, is believed to reflect the different environments of the nitrogen atoms. Similar observations have been reported for other
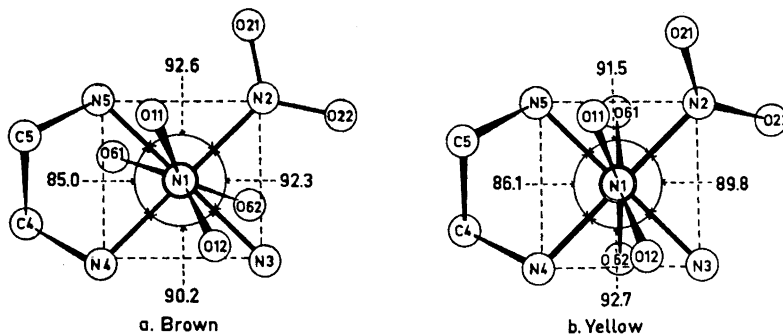

Fig. 3. The two forms of [Co(NO$_2$)$_2$NH$_3$en] viewed perpendicularly to the least squares plane through N2, N3, N4, N5 showing the bond angles in the plane.

Table 4. Bond angles and standard deviations.

a. Brown form			b. Yellow form		
Atoms	Angles	(degrees)	Atoms	Angles	(degrees)
N1 —Co —N2	87.1	(0.2)	N1 —Co —N2	91.8	(0.3)
N1 —Co —N3	90.2	(0.2)	N1 —Co —N3	89.9	(0.3)
N1 —Co —N4	91.6	(0.2)	N1 —Co —N4	90.9	(0.3)
N1 —Co —N5	90.7	(0.2)	N1 —Co —N5	89.3	(0.3)
N2 —Co —N3	92.3	(0.3)	N2 —Co —N3	89.8	(0.3)
N2 —Co —N5	92.6	(0.3)	N2 —Co —N5	91.5	(0.3)
N2 —Co —N6	89.5	(0.2)	N2 —Co —N6	88.9	(0.3)
N3 —Co —N4	90.2	(0.3)	N3 —Co —N4	92.7	(0.3)
N3 —Co —N6	89.0	(0.2)	N3 —Co —N6	90.7	(0.3)
N4 —Co —N5	85.0	(0.3)	N4 —Co —N5	86.1	(0.3)
N4 —Co —N6	91.8	(0.2)	N4 —Co —N6	88.4	(0.3)
N5 —Co —N6	90.5	(0.2)	N5 —Co —N6	90.1	(0.3)
O11—N1—O12	117.0	(0.7)	O11—N1—O12	117.7	(0.7)
O21—N2—O22	117.8	(0.6)	O21—N2—O22	120.6	(0.7)
Co —N4—C4	110.5	(0.4)	Co —N4—C4	109.0	(0.5)
Co —N5—C5	109.7	(0.4)	Co —N5—C5	109.8	(0.5)
O61—N6—O62	117.0	(0.5)	O61—N6—O62	120.2	(0.7)
N4 —C4 —C5	107.6	(0.6)	N4 —C4 —C5	106.0	(0.7)
C4 —C5 —N5	106.5	(0.5)	C4 —C5 —N5	106.4	(0.6)
Co —N3—H31	106.9	(5.)	Co —N3—H31	119.0	(6.)
Co —N3—H32	109.9	(5.)	Co —N3—H32	116.1	(6.)
Co —N3—H33	114.1	(5.)	Co —N3—H33	116.1	(7.)
Co —N4—H41	112.6	(5.)	Co —N4—H41	116.0	(6.)
Co —N4—H42	111.2	(4.)	Co —N4—H42	116.3	(6.)
Co —N5—H51	116.6	(5.)	Co —N5—H51	99.7	(6.)
Co —N5—H52	111.1	(4.)	Co —N5—H52	96.6	(6.)
C4 —N4—H41	109.8	(4.)	C4 —N4—H41	104.0	(6.)
C4 —N4—H42	113.3	(4.)	C4 —N4—H42	105.6	(6.)
C5 —N5—H51	105.6	(4.)	C5 —N5—H51	119.7	(6.)
C5 —N5—H52	105.2	(4.)	C5 —N5—H52	114.0	(6.)
C5 —C4 —H43	112.9	(4.)	C5 —C4 —H43	105.2	(6.)
C5 —C4 —H44	117.6	(4.)	C5 —C4 —H44	110.7	(5.)
C4 —C5 —H53	109.4	(4.)	C4 —C5 —H53	108.5	(6.)
C4 —C5 —H54	102.6	(4.)	C4 —C5 —H54	120.1	(5.)

Table 5. Distances (in Å) from the least squares plane through N2, N3, N4, N5. The distances to the nitro groups (1) and (6) are omitted.

Atom	a. Brown from	b. Yellow form
N2	0.016	—0.030
N3	—0.016	0.029
N4	0.017	—0.030
N5	—0.017	0.030
Co	—0.006	0.017
O21	0.086	0.468
O22	0.028	—0.624
C4	—0.251	—0.444
C5	0.399	0.293
H31	0.27	0.72
H32	—0.80	—0.84
H33	0.60	0.26
H41	0.80	0.83
H42	—0.60	—0.64
H51	0.53	0.66
H52	—0.97	—0.89
H43	0.07	—0.24
H44	—1.29	—1.59
H53	1.37	1.31
H54	—0.08	0.06

Table 6. O···H distances in the complex shorter than 3.30 Å and standard deviations.

| | a. Brown form | | b. Yellow form | |
Atoms	Distances (Å)	(σ)	Distances (Å)	(σ)
O11—H51	2.48	(9)	2.26	(11)
O11—H53	2.66	(9)	2.85	(10)
O12—H31	2.77	(8)	2.62	(11)
O12—H33	2.36	(8)	2.70	(11)
O12—H41	2.82	(9)	2.76	(11)
O21—H51	2.47	(7)	2.26	(10)
O21—H52	2.98	(8)	2.90	(11)
O22—H31	2.24	(8)	2.79	(11)
O22—H32	3.28	(8)	2.83	(11)
O61—H42	3.22	(8)		
O61—H44	2.63	(7)	3.11	(10)
O61—H52	2.19	(8)	2.13	(11)
O62—H31	3.10	(9)		
O62—H32	2.33	(9)	2.48	(11)
O62—H33			3.18	(11)
O62—H42			2.53	(10)
O62—H44			2.85	(11)

Table 7. X—H···O [Q] (X=N or C) distances shorter than 3.30 Å are listed.

| Atoms | Q | Distances (Å) | | | Angle (°) |
X—H···O		X···O	X—H	H···O	XHO
a. Brown form					
N3—H33···O21	[3]	3.05	0.83	2.40	135
N4—H41···O21		3.09	0.91	2.59	116
— H42 —		—	0.99	2.67	106
N3—H32···O22	[4]	3.28	0.88	2.56	139
N3—H31···O62		3.12	0.87	2.41	140
N3—H32···O61	[5]	3.22	0.88	2.48	142
N4—H42···O61		3.19	0.99	2.27	154
— — O62		3.02	—	2.22	137
C4 —H44···O62		3.20	1.05	2.66	112
C5 —H53···O12	[8]	3.08	0.98	2.68	105
N5—H51···O12		3.18	0.91	2.47	135
N4—H41···O11	[9]	2.97	0.91	2.16	149
b. Yellow form					
N5—H52···O62	[2]	3.23	0.97	2.46	135
N3—H32···O61	[5]	3.02	0.97	2.07	164
N3—H33···O21	[6]	3.23	0.84	2.47	150
— — O22		3.13	—	2.35	155
N4—H42···O22		3.10	0.96	2.51	121
N4—H42···O62	[7]	3.16	0.96	2.47	128
N5—H51···O12	[8]	3.29	0.94	2.54	137
N3—H31···O11	[9]	3.17	1.04	2.19	156
N4—H41···O12	[10]	3.01	0.99	2.10	154

Note: Q = [2]: $2-x$, $0.5+y$, $1.5-z$ [7]: $2-x$, $1-y$, $1-z$
    [3]: x, $y-1$, z [8]: $1-x$, $0.5+y$, $1.5-z$
    [4]: $2-x$, $1-y$, $2-z$ [9]: $1-x$, $y-0.5$, $1.5-z$
    [5]: $2-x$, $y-0.5$, $1.5-z$ [10]: $1-x$, $1-y$, $1-z$
    [6]: x, $0.5-y$, $z-0.5$

Co(III)-complexes. In nitropentamminecobalt(III) bromide Cotton and Edwards[2] found a Co—N (nitro) bond length of 1.921 Å (e.s.d. 0.021 Å) and an average Co—N (ammine) bond length of 1.978 Å. The lengths of the same bonds were determined by Börtin[3] in nitropentamminecobalt(III) chloride to 1.912 Å (e.s.d. 0.014 Å) and 1.961 Å (average), respectively.

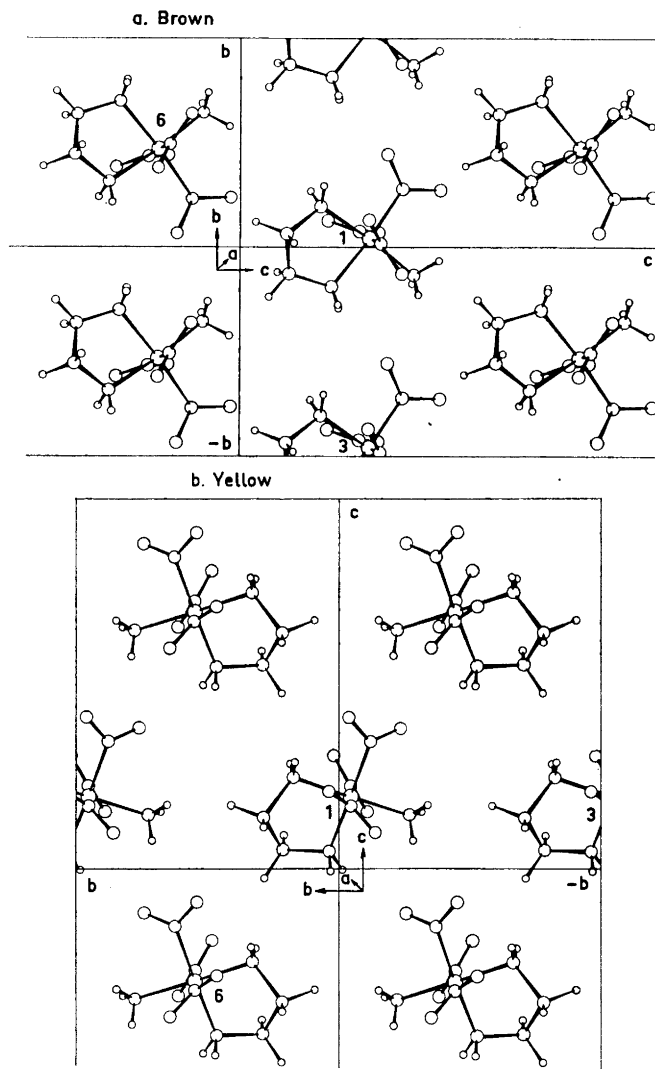The Co—N4 bond length (Table 3 and Fig. 1) is significantly larger than the Co—N5 bond length. The differences are 5 e.s.d. (brown form) and 3 e.s.d.

Fig. 4. (100) projections of the two structures.

(yellow form). A stronger *trans* effect of a nitro group than of ammonia may account for this observation.

The bond angles N—Co—N are close to 90° as shown in Table 4 and Fig. 3. The smallest angle, N4—Co—N5, is found in the chelate ring, *viz.* 85.0° in the brown form and 86.1° in the yellow one. Angles of approximately 86° are also observed in *trans*-dichlorobisethylenediaminecobalt(III) nitrate (Ooi and Kuroya [4]) and in tris(*l*-propylenediamine)cobalt(III) bromide (Iwasaki and Saito [5]).

The packing efficiencies of the two isomers are virtually identical. The packing arrangements, however, are somewhat different as shown in Fig. 4, a and b. N—H$\cdots$O(C—H$\cdots$O) distances shorter than 3.30 Å are listed in Table 7. It is noticeable that in both structures each oxygen is found to have at least one N—H$\cdots$O distance shorter than 3.30 Å. The N—H$\cdots$O (C—H$\cdots$O) and H$\cdots$O distances are gradually increasing. Hence, it may be difficult to distinguish sharply between hydrogen bonds and van der Waals contacts.

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