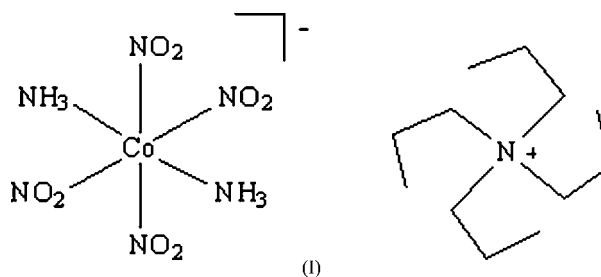


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Key indicators

Single-crystal X-ray study
T = 295 K
Mean $\sigma(\text{C}-\text{C}) = 0.007 \text{ \AA}$
R factor = 0.051
wR factor = 0.137
Data-to-parameter ratio = 19.1For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Tetrapropylammonium *trans*-diammine-
tetrannitrocobaltate(III)The Co^{III} title complex, $[(\text{C}_3\text{H}_7)_4\text{N}][\text{trans-Co}(\text{NH}_3)_2(\text{NO}_2)_4]$, has been synthesized and crystallized from an acetone–water mixture. The asymmetric unit contains two cations and two anions. The X-ray structure determination revealed the presence of discrete ions interacting through weak hydrogen bonds and van der Waals interactions, as well as Coulombic interactions.Received 27 June 2006
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Comment

 Co^{III} complexes continue to receive attention owing to their pivotal role in the development of inorganic chemistry. Throughout their eventful historical development they were and still are key compounds in such diverse study areas as synthesis, coordination geometry and isomerism, spectroscopy (optical and NMR), conformational analysis and redox processes. Moreover, a Co^{III} centre is present in vitamin B12 and Co^{III} complexes are used as catalysts in the synthesis and hydrolysis of peptides (Browne *et al.*, 2000).In continuation of our interest in the structural chemistry of salts containing the ion $[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]^-$ (Sharma, Sharma, Bala, Vermani *et al.*, 2006; Sharma, Sharma, Bala, Gill *et al.*, 2006), this paper reports the synthesis, spectroscopic characterization and single-crystal X-ray structure determination of the complex salt $[(\text{C}_3\text{H}_7)_4\text{N}][\text{trans-Co}(\text{NH}_3)_2(\text{NO}_2)_4]^-$, (I). Our aim is to understand the effect of the cation on the physicochemical properties of these salts.An *ORTEP* (Burnett & Johnson, 1996) view of (I) is shown in Fig. 1. The asymmetric unit is formed by two Co^{III} complexes and two tetrapropylammonium cations. The Co^{III} centres, *trans*-coordinated by two ammonia molecules and four nitro groups, adopt an almost perfect octahedral geometry (Table 1). The $\text{Co}-\text{N}(\text{ammonia})$ and $\text{Co}-\text{N}(\text{nitro})$ bond lengths range from 1.914 (3) to 1.951 (3) Å and from 1.927 (4) to 1.966 (4) Å, respectively, in agreement with the values found in other diamminotetrannitro- Co^{III} complexes (Bondar *et al.*, 1979, 1980; Rau *et al.*, 1982; Bernal, 1985; Bernal & Cetrullo, 1989; Kofod *et al.*, 1997; Sharma, Sharma,

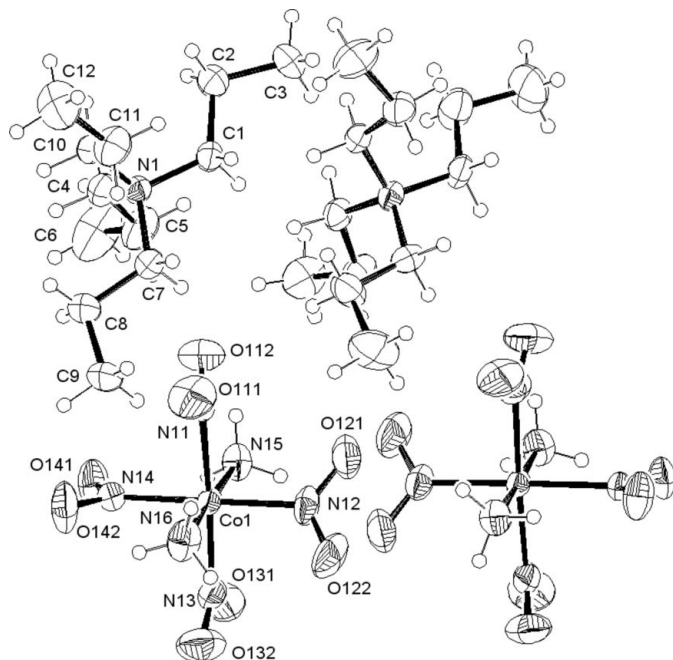


Figure 1
ORTEP view of the asymmetric unit of (I), with ellipsoids drawn at the 40% probability level. For the sake of clarity, the atom numbering is given only for one cation/anion couple.

Bala, Vermani *et al.*, 2006). As for the tetrapropylammonium cations, the geometry around the central N atoms is regular tetrahedral (Table 1).

The main intermolecular interactions involved in the crystal structure, besides van der Waals interactions, are weak N—H...O and C—H...O hydrogen bonds (Table 2). As a general rule, we have considered the C—H...X (X = N and O) interactions where the H...X distance is less than 2.70 Å and C—H...X angle is greater than 130° to be significant. The cell contents, viewed down the *b* axis, are shown in Fig. 2.

Experimental

Analytical grade reagents were used without any further purification. K[*trans*-Co(NH₃)₂(NO₂)₄] was prepared according to the method described by Schlessinger (1967). Potassium *trans*-diamminetetranitrocobaltate(III) (1.00 g, 3 mmol) was dissolved in 35 ml of hot water by mechanical stirring for 10–15 min. In another beaker, tetrapropylammonium bromide (0.84 g, 3 mmol) was dissolved in a minimum amount of water (10 ml). The solutions were then mixed with stirring and a yellow solid precipitated immediately. This product was washed with ice-cold water and air-dried. Yellow single crystals suitable for X-ray structure determination were obtained from an acetone–water mixture (30% *v/v* acetone; yield 87%). The complex salt is stable in air and light, soluble in water, and highly soluble in acetone and dimethylsulfoxide (m.p. 465 K). Analysis, found: C 31.1, H 7.3, N 21.1, Co 12.7%; calculated for C₁₂H₃₄CoN₇O₈: C 31.0, H 7.3, N 21.1, Co 12.7%. IR (KBr, cm⁻¹): ν_{as}(NH₃⁻) 3343, ν_s(NH₃⁻) 3235, ν_{as}(NH₃) 1633, ν_{as}(-NO₂⁻) 1422, ν_{as}(-NO₂⁻) 1317. UV–vis (nm): 352, 252. ¹H NMR (300 MHz, DMSO-*d*₆): δ 0.988 (12H, 4 CH₃), 1.65 (8H, 4 CH₂), 3.11 (8H, 4 CH₂—N), 3.88 (6H, 2 NH₃).

Crystal data

(C₁₂H₂₈N)[Co(NO₂)₄(NH₃)₂]
M_r = 463.39
Orthorhombic, *Pca*2₁
a = 23.4483 (1) Å
b = 8.5304 (4) Å
c = 22.5347 (5) Å
V = 4507.5 (2) Å³

Z = 8
D_x = 1.366 Mg m⁻³
Mo Kα radiation
μ = 0.81 mm⁻¹
T = 295 K
Prism, yellow
0.45 × 0.29 × 0.17 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan
(*SORTAV*; Blessing, 1995)
*T*_{min} = 0.768, *T*_{max} = 0.865

22694 measured reflections
9899 independent reflections
7560 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.044
θ_{max} = 28°

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.051
wR (*F*²) = 0.137
S = 1.03
9899 reflections
518 parameters

H-atom parameters constrained
w = 1/[σ²(*F*_o²) + (0.0814*P*)²]
where *P* = (*F*_o² + 2*F*_c²)/3
(Δσ)_{max} = 0.001
Δρ_{max} = 0.57 e Å⁻³
Δρ_{min} = -0.65 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Co1—N11	1.956 (4)	Co2—N25	1.938 (3)
Co1—N12	1.927 (4)	Co2—N26	1.951 (3)
Co1—N13	1.943 (4)	N1—C1	1.520 (4)
Co1—N14	1.944 (4)	N1—C4	1.517 (5)
Co1—N15	1.936 (3)	N1—C7	1.517 (4)
Co1—N16	1.914 (3)	N1—C10	1.522 (4)
Co2—N21	1.959 (4)	N2—C13	1.512 (4)
Co2—N22	1.966 (4)	N2—C16	1.517 (4)
Co2—N23	1.934 (4)	N2—C19	1.524 (4)
Co2—N24	1.937 (4)	N2—C22	1.519 (4)
N16—Co1—N12	89.75 (19)	N25—Co2—N21	90.31 (18)
N12—Co1—N15	89.18 (18)	N26—Co2—N21	88.52 (17)
N16—Co1—N13	90.25 (19)	N23—Co2—N22	88.33 (16)
N12—Co1—N13	92.36 (16)	N25—Co2—N22	91.27 (16)
N15—Co1—N13	89.56 (17)	N26—Co2—N22	90.61 (16)
N16—Co1—N14	90.04 (17)	N21—Co2—N22	88.69 (16)
N15—Co1—N14	91.03 (15)	C7—N1—C4	111.2 (3)
N13—Co1—N14	87.79 (16)	C7—N1—C1	106.2 (3)
N16—Co1—N11	91.09 (17)	C4—N1—C1	111.4 (3)
N12—Co1—N11	91.09 (18)	C7—N1—C10	110.9 (3)
N15—Co1—N11	89.17 (16)	C4—N1—C10	106.3 (3)
N14—Co1—N11	88.76 (16)	C1—N1—C10	110.9 (3)
N23—Co2—N24	90.72 (18)	C13—N2—C16	110.5 (3)
N23—Co2—N25	90.49 (17)	C13—N2—C22	105.8 (2)
N24—Co2—N25	88.83 (18)	C16—N2—C22	112.0 (3)
N23—Co2—N26	90.77 (16)	C13—N2—C19	110.6 (3)
N24—Co2—N26	89.31 (18)	C16—N2—C19	106.5 (3)
N24—Co2—N21	92.25 (16)	C22—N2—C19	111.5 (3)

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>
N15—H151...O242	0.89	2.28	3.143 (5)	165
N25—H253...O122 ⁱ	0.89	2.30	3.096 (5)	149
N26—H263...O121	0.89	2.35	3.169 (5)	153
C4—H42...O221 ⁱⁱ	0.97	2.61	3.498 (5)	153
C10—H101...O131 ⁱⁱⁱ	0.97	2.46	3.396 (5)	164
C14—H141...O131 ^{iv}	0.97	2.63	3.493 (6)	148
C16—H165...O141 ^{iv}	0.97	2.60	3.439 (5)	145

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C19—H191 \cdots O212	0.97	2.44	3.398 (5)	169
C19—H192 \cdots O141 ^{iv}	0.97	2.63	3.493 (6)	148

Symmetry codes: (i) $x, y + 1, z$; (ii) $-x + \frac{1}{2}, y, z - \frac{1}{2}$; (iii) $x - \frac{1}{2}, -y + 1, z$; (iv) $-x + \frac{1}{2}, y, z + \frac{1}{2}$.

A BASF/TWIN type of refinement was used obtaining a final BASF value (*i.e.* the fractional contribution of the inverted structure) of 0.30. 4373 Friedel pairs were used for the analysis. The structure was refined with the crystal treated as an inversion twin. H atoms were placed in idealized positions and refined as riding on their parent atoms; constrained distances: 0.97 (methylene CH₂), 0.96 (methyl CH₃) and 0.89 Å (ammonia NH₃). Isotropic parameters for H atoms were fixed at $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier atom})$.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL97* and *WinGX* (Farrugia, 1999).

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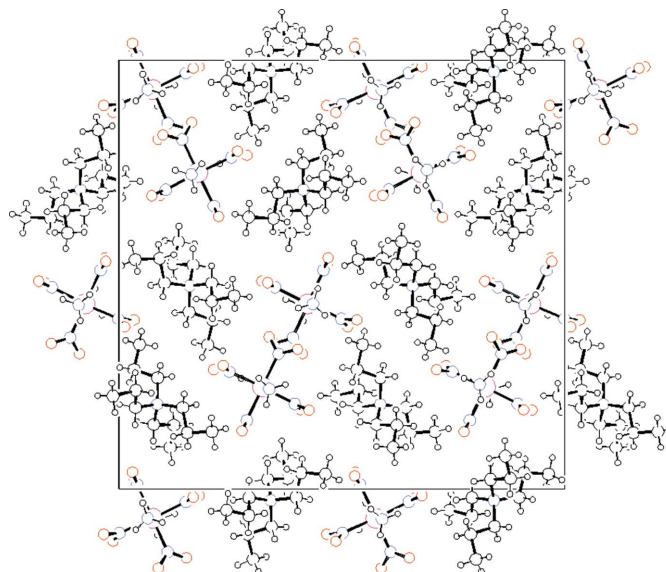


Figure 2

A packing diagram of the title compound, viewed along [010].

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