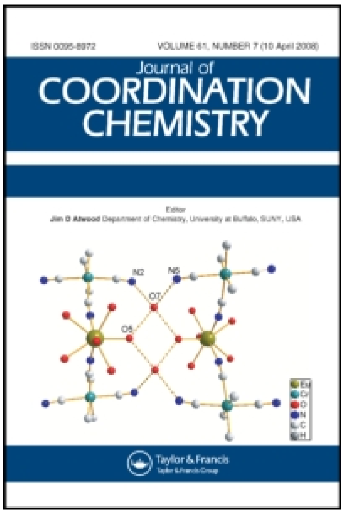


**Journal of Coordination Chemistry**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

# Synthesis, spectroscopic characterization and X-ray crystal structure determination of trialkylbenzylammonium *trans*-diamminetetranitrocobaltate(III) salts where alkyl = methyl and ethyl

Raj Pal Sharma[a]; Ritu Bala[a]; Rajni Sharma[a]; Bal Krishan Vermani[a]; Dip Singh Gill[a]; Paloth Venugopalan[a]
[a] Chemistry Department, Panjab University, Chandigarh 160 014, India

**To cite this Article** Sharma, Raj Pal , Bala, Ritu , Sharma, Rajni , Vermani, Bal Krishan , Gill, Dip Singh and Venugopalan, Paloth(2005) 'Synthesis, spectroscopic characterization and X-ray crystal structure determination of trialkylbenzylammonium *trans*-diamminetetranitrocobaltate(III) salts where alkyl = methyl and ethyl', Journal of Coordination Chemistry, 58: 4, 309 — 316

**To link to this Article: DOI:** 10.1080/00958970512331325557

**URL:** http://dx.doi.org/10.1080/00958970512331325557

*Journal of Coordination Chemistry*
Vol. 58, No. 4, 10 March 2005, 309–316

# Synthesis, spectroscopic characterization and X-ray crystal structure determination of trialkylbenzylammonium *trans*-diamminetetranitrocobaltate(III) salts where alkyl = methyl and ethyl

RAJ PAL SHARMA*, RITU BALA, RAJNI SHARMA,
BAL KRISHAN VERMANI, DIP SINGH GILL and PALOTH VENUGOPALAN

Chemistry Department, Panjab University, Chandigarh 160 014, India

*(Received 8 January 2004; In final form 8 May 2004)*

The two cobalt(III) complex salts $[(CH_3)_3NCH_2C_6H_5][\textit{trans}\text{-}Co(NH_3)_2(NO_2)_4]$ and $[(C_2H_5)_3NCH_2C_6H_5][\textit{trans}\text{-}Co(NH_3)_2(NO_2)_4]$ have been synthesized by reacting $[(CH_3)_3NCH_2C_6H_5]Cl$ and $[(C_2H_5)_3NCH_2C_6H_5]Cl$, respectively, with $K[\textit{trans}\text{-}Co(NH_3)_2(NO_2)_4]$, in aqueous medium at room temperature. The salt $[(C_2H_5)_3NCH_2C_6H_5][\textit{trans}\text{-}Co(NH_3)_2(NO_2)_4]$ crystallized from an acetone–water mixture; monoclinic, space group $P2_1/n$, cell dimensions $a = 10.620(1)$, $b = 14.954(1)$, $c = 14.100(1)$ Å, $\beta = 109.88°$, $V = 2105.8(3)$ Å$^3$, $Z = 4$. An X-ray structure determination revealed the presence of discrete ions $[(C_2H_5)_3NCH_2C_6H_5]^+$ and $[\textit{trans}\text{-}Co(NH_3)_2(NO_2)_4]^-$ in the structure. In the anion cobalt(III) is coordinated octahedrally with the expected *trans* geometry.

*Keywords:* Cobalt(III); Organic cations; Spectroscopy; X-ray crystallography; Nitro; Amine

## 1. Introduction

Cobalt(III) complexes continue to receive attention [1–4] because of their pivotal role in the development of inorganic chemistry, the presence of a cobalt(III) center in vitamin $B_{12}$ and the use of cobalt(III) complexes as catalysts in the synthesis and hydrolysis of peptides [5–6]. In continuation of our interest [7–15] in cobalt(III) salts, this article reports the synthesis and characterization of the salts $[(CH_3)_3NCH_2C_6H_5][\textit{trans}\text{-}Co(NH_3)_2(NO_2)_4]$ and $[(C_2H_5)_3NCH_2C_6H_5][\textit{trans}\text{-}Co(NH_3)_2(NO_2)_4]$. The yellow salts were synthesized by reaction of benzyltrimethylammonium chloride and benzyltriethylammonium chloride with potassium *trans*-diamminotetranitrocobaltate(III) in a 1:1 mole ratio in aqueous medium. The newly synthesized salts have been characterized

---

*Corresponding author. E-mail: rpsharmapu@yahoo.com

*Journal of Coordination Chemistry*
ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970512331325557

on the basis of elemental analyses, spectroscopic studies and a single-crystal X-ray structure determination.

## 2. Experimental

### 2.1. *Materials*

Analytical grade reagents were used without further purification. K[*trans*-Co$(NH_3)_2$$(NO_2)_4$] was prepared according to the method described by Schlessinger [16].

### 2.2. *Instrumentation*

Cobalt was determined by standard methods and C, H and N were estimated microanalytically with a Perkin Elmer 2400CHN instrument. Electronic spectra were recorded using a Hitachi 330 spectrophotometer with water and DMSO as solvents. Infrared spectra of the salts were recorded using a Perkin Elmer RX FT-IR system with Nujol mulls and HCB suspension between KBr plates. $^1$H NMR and $^{13}$C NMR spectra were run in acetone-$d_6$ and DMSO-$d_6$ using a Brucker AC 300 F (300 MHz) spectrometer. The chemical shift values are expressed as $\delta$ values (ppm) downfield from tetramethylsilane as internal standard.

### 2.3. $[(CH_3)_3NCH_2C_6H_5][trans\text{-}Co(NH_3)_2(NO_2)_4]$

Potassium *trans*-diamminetetranitrocobaltate(III) was dissolved in 40 cm$^3$ of hot water with mechanical stirring for 10–15 min. In another beaker 0.58 g of benzyltrimethylammonium chloride was dissolved in a minimum amount of hot water (10 cm$^3$). The solutions were mixed together with stirring and a yellow solid precipitated immediately, which was washed with ice-cold water and air dried. Orange single crystals suitable for X-ray structure determination were obtained from an acetone–water mixture. The yield was 88%.

### 2.4. $[(C_2H_5)_3NCH_2C_6H_5][trans\text{-}Co(NH_3)_2(NO_2)_4]$

Potassium *trans*-diamminetetranitrocobaltate(III) was dissolved in 40 cm$^3$ of hot water by mechanical stirring for 10–15 min. In another beaker 0.72 g of benzyltriethylammonium chloride was dissolved in a minimum amount of hot water (10 cm$^3$). The solutions were mixed together with stirring and a yellow solid precipitated immediately, which was washed with ice-cold water and air dried. The yield was 89%.

### 2.5. *Crystallography*

Orange single crystals of $[(C_2H_5)_3NCH_2C_6H_5]$[*trans*-Co$(NH_3)_2(NO_2)_4$] suitable for X-ray diffraction studies were grown from acetone–water solution by slow evaporation. A single crystal with dimensions 0.29 × 0.19 × 0.18 mm was mounted along the largest dimension and used for data collection. Intensity data were collected on a Siemens P4 single-crystal diffractometer equipped with a molybdenum tube ($\lambda = 0.71073$ Å) and a highly oriented graphite monochromator. Lattice parameters and standard deviations

Table 1. Crystal data and structure refinement details for $[(C_2H_5)_3NCH_2C_6H_5][\textit{trans}\text{-}Co(NH_3)_2(NO_2)_4]$.

| | |
|---|---|
| Empirical formula | $C_{13}H_{28}CoN_7O_8$ |
| Formula weight | 469.35 |
| Temperature | 293(2) $K$ |
| Diffractometer used | Siemens P4 |
| Radiation used, Wavelength | Mo K$\alpha$, 0.71073 Å |
| Crystal system, Space group | Monoclinic, $P2_1/n$ |
| Unit cell dimensions | $a = 10.260(1)$ Å<br>$b = 14.954(1)$ Å $\beta = 109.88°$<br>$c = 14.100(1)$ Å |
| Volume | 2105.3(3) Å$^3$ |
| $Z$ and density (calculated) | 4, 1.480 Mg m$^{-3}$ |
| Absorption coefficient | 0.869 mm$^{-1}$ |
| $F$(000) | 984 |
| Crystal size | $0.29 \times 0.19 \times 0.18$ mm |
| Max. and min. transmission | 0.877, 0.805 |
| $\theta$ range of data collection | 2.05 to 24.00° |
| Scan type | $2\theta$–$\theta$ |
| Index ranges | $0 \le h \le 12$, $-17 \le k \le 0$, $-16 \le l \le 15$ |
| Reflections collected | 3509 |
| Independent reflections | 3302 ($R_{\text{int}} = 0.0148$) |
| Refinement method | Full-matrix least-square on $F^2$ |
| Data/restraints/parameters | 3302/0/266 |
| Goodness-of-fit on $F^2$, ($S$) | 1.034 |
| Weighting scheme | $1/[\sigma^2(FF_o^2) + (0.0407P)^2 + 1.47P]$,<br>$P = (\max(F_o^2, 0) + 2F_c^2)/3$ |
| Data to parameter ratio | 12.4 : 1 |
| Final $R$ indices, 288 reflection [$I > 2\sigma(I)$] | $R1 = 0.0355$, $wR2 = 0.0883$ |
| $R$ indices (all data) | $R1 = 0.0512$, $wR2 = 0.0984$ |
| Extinction coefficient | 0.0126(6) |
| Largest diff. peak and hole | 0.481 and −0.419 e Å$^{-3}$ |

were obtained by a least-squares fit to 40 reflections. Data were collected by the $2\theta$–$\theta$ scan mode with variable scan speeds ranging from 2.0° to a maximum of 60.0° per minute. Data were corrected for Lorentz and polarization factors and an empirical absorption correction based on psi scans was applied. All other relevant information on data collection is presented in table 1. Atomic coordinates of nonhydrogen atoms are given in table 2. The structure was solved and refined by direct methods using the SHELX-97 package [17].

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 231389. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (44) 1223 336-033; e-mail: deposit@ccdc.cam.ac.uk].

## 3. Results and discussion

$[(CH_3)_3NCH_2C_6H_5][\textit{trans}\text{-}Co(NH_3)_2(NO_2)_4]$ and $[(C_2H_5)_3NCH_2C_6H_5][\textit{trans}\text{-}Co(NH_3)_2(NO_2)_4]$ salts were synthesized and characterized on the basis of elemental analyses, spectroscopic studies and a single-crystal X-ray structure determination. The literature reports two transitions $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ at around 470 and 340 nm, respectively, producing the familiar orange–yellow color for a number of classical

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for $[(C_2H_5)_3NCH_2C_6H_5]$[*trans*-$Co(NH_3)_2(NO_2)_4$].

| | *x*/*a* | *y*/*b* | *z*/*c* | *U*(eq) |
|---|---|---|---|---|
| Co(1) | 5000 | 0 | 5000 | 28(1) |
| Co(2) | 0 | 0 | 0 | 30(1) |
| O(1) | 2774(4) | −553(2) | 5411(4) | 143(2) |
| O(2) | 3160(3) | 780(2) | 5748(2) | 93(1) |
| O(3) | 6998(2) | −638(2) | 6701(2) | 72(1) |
| O(4) | 6396(3) | 685(2) | 6899(2) | 88(1) |
| O(5) | 7254(2) | −14(2) | 9534(2) | 81(1) |
| O(6) | 8255(2) | 455(2) | 11 005(2) | 77(1) |
| O(7) | 10 481(3) | 1720(2) | 9465(2) | 85(1) |
| O(8) | 10 546(3) | 1657(2) | 10 976(2) | 69(1) |
| N(1) | 4268(2) | 2443(1) | 8338(2) | 36(1) |
| N(2) | 3490(2) | 87(2) | 5472(2) | 47(1) |
| N(3) | 6276(2) | 21(2) | 6365(2) | 45(1) |
| N(4) | 5077(2) | 1289(2) | 4935(2) | 52(1) |
| N(5) | 8308(2) | 160(2) | 10 211(2) | 45(1) |
| N(6) | 10 384(2) | 1280(2) | 10 170(2) | 45(1) |
| N(7) | 9142(3) | 176(2) | 8572(2) | 50(1) |
| C(1) | 1818(3) | 2516(2) | 7115(2) | 43(1) |
| C(2) | 1169(3) | 3321(2) | 7116(3) | 60(1) |
| C(3) | −190(4) | 3346(3) | 6937(3) | 78(1) |
| C(4) | −928(4) | 2564(3) | 6740(3) | 75(1) |
| C(5) | −303(3) | 1763(3) | 6720(3) | 64(1) |
| C(6) | 1058(3) | 1739(2) | 6902(2) | 52(1) |
| C(7) | 3289(3) | 2497(2) | 7252(2) | 41(1) |
| C(8) | 3934(3) | 1648(2) | 8886(2) | 48(1) |
| C(9) | 4133(3) | 740(2) | 8483(3) | 63(1) |
| C(10) | 5658(3) | 2356(2) | 8266(3) | 48(1) |
| C(11) | 6781(3) | 2312(2) | 9260(3) | 66(1) |
| C(12) | 4163(3) | 3269(2) | 8936(2) | 47(1) |
| C(13) | 4600(4) | 4140(2) | 8595(3) | 60(1) |

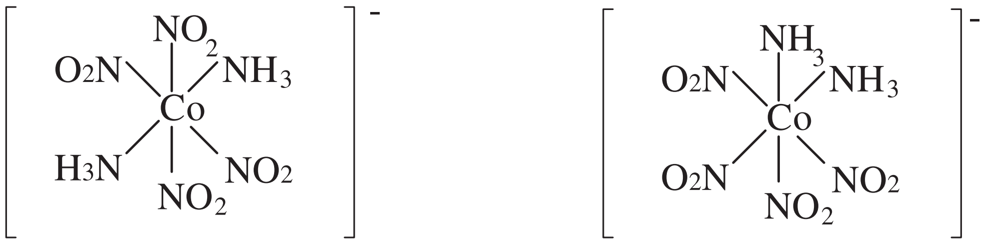
coordination compounds containing cobalt(III) [18]. A special absorption [19] due to the nitro group appears in the region 350 to 330 nm. The second absorption usually found in cobalt(III) complexes is strongly masked. Thus the absorption curves are quite different from those of $[Co(NH_3)_6]^{3+}$, $[Co(en)_3]^{3+}$ and $[Co(NH_3)_5\ Cl]^{2+}$. The two nitro groups coordinate to the cobalt atom in *trans* positions, and a third absorption band appears at approximately 250 nm [20–22]. A similar phenomenon has been observed in the title salts in aqueous medium as reported in table 3. Electronic spectra of K[*trans*-$Co(NH_3)_2(NO_2)_4$], $[(CH_3)_3NCH_2C_6H_5]$[*trans*-$Co(NH_3)_2(NO_2)_4$] and $[(C_2H_5)_3NCH_2C_6H_5]$[*trans*-$Co(NH_3)_2(NO_2)_4$] recorded in DMSO were found to be identical, within experimental error.

Assignment of the IR bands of [*trans*-$Co(NH_3)_2(NO_2)_4]^-$ anion was done on the basis of well-established previous work [23]. The antisymmetric stretching modes of $NH_3$ and $NO_2$ appear at 3262 and 1426 cm$^{-1}$, respectively. The symmetric stretching mode of $NO_2$ appears at 1314 cm$^{-1}$. For $[(CH_3)_3NCH_2C_6H_5]^+$ and $[(C_2H_5)_3NCH_2C_6H_5]^+$ assignments were made on the basis of well-established literature values [24] and are given in table 3.

$^1$H NMR and $^{13}$C NMR data for both salts in acetone and DMSO at 25°C are given in table 3 [25–27].

Table 3. Analytical and spectroscopic data for $[(CH_3)_3NCH_2C_6H_5][\textit{trans}\text{-}Co(NH_3)_2(NO_2)_4]$ and $[(C_2H_5)_3NCH_2C_6H_5][\textit{trans}\text{-}Co(NH_3)_2(NO_2)_4]$.

| | $[(CH_3)_3NCH_2C_6H_5][Co(NH_3)_2(NO_2)_4]$ | $[(C_2H_5)_3NCH_2C_6H_5][Co(NH_3)_2(NO_2)_4]$ |
|---|---|---|
| Melting point (°C) | 180 | 201 |
| Elemental analyses: Calcd. (Found) | | |
| Co | 13.79 (13.72) | 12.56 (12.76) |
| C | 28.10 (28.20) | 33.24 (33.34) |
| H | 5.15 (5.20) | 5.97 (5.99) |
| N | 22.9 (23.01) | 20.89 (20.98) |
| UV/visible (nm) | 348, 253 | 348, 253 |
| IR (HCB) ($cm^{-1}$) | | |
| $\nu_a(NH_3)$ | 3257 | 3262 |
| $\nu_s(ArH)$ | 3036 | 3026 |
| $\nu_s(CH_3)$ | 2958 | 2962 |
| $\nu_{as}(CH_2)$ | 2926 | 2926 |
| $\nu_s(CH_2)$ | 2854 | 2854 |
| $\nu_s(C{=}C)$ | 1611 | 1611 |
| $\nu_{as}(NO_2)$ | 1420 | 1429 |
| $\nu_s(NO_2)$ | 1317 | 1314 |
| | Acetone-$d_6$ | DMSO-$d_6$ |
| $^1H$ NMR $\delta$ (ppm) | 7.6 (m, 5H, Ar-H), 4.7 (s, 2H, $-CH_2$), 3.29 (s, 6H, $2NH_3$), 2.1 (s, 9H, $CH_3$) | 7.5 (m, 5H, Ar-H), 4.5 (s, 2H, $-CH_2$), 3.45 (q, 6H, $-CH_2-$) 3.1 (s, 6H, $NH_3$), 1.44 (t, 9H, $CH_3$) 127–132 |
| $^{13}C$ NMR $\delta$ (ppm) | 130–134 (Ar-C), 70.4 ($-CH_2$), 53.5 ($CH_3$) | 130–134 (Ar-C), 59.44 ($-CH_2$), 51.97 ($-CH_2-$), 7.44 ($CH_3$) |



(A) (A')

Figure 1. Octahedral isomers of $[Co(NH_3)_2(NO_2)_4]^-$, *trans*- (A) and *cis*- (B).

## 3.1. *X-ray crystal structure*

The crystal structure of the benzyltriethylammonium diamminetetranitrocobaltate(III) complex salt was determined. As the disubstituted octahedral complex has two stereoisomers, *trans* and *cis* forms, there exist two possibilities as shown in figure 1.

The X-ray structure determination confirmed the composition and the existence of the independent ions $[(C_2H_5)_3NCH_2C_6H_5]^+$ and $[Co(NH_3)_2(NO_2)_4]^-$ (two lying across centers). An ORTEP diagram is shown in figure 2. The structure is stabilized by electrostatic forces and hydrogen bonding. Bond lengths and angles for the anions are comparable with those in $K[\textit{trans}\text{-}Co(NH_3)_2(NO_2)_4]$ (**I**) [28],

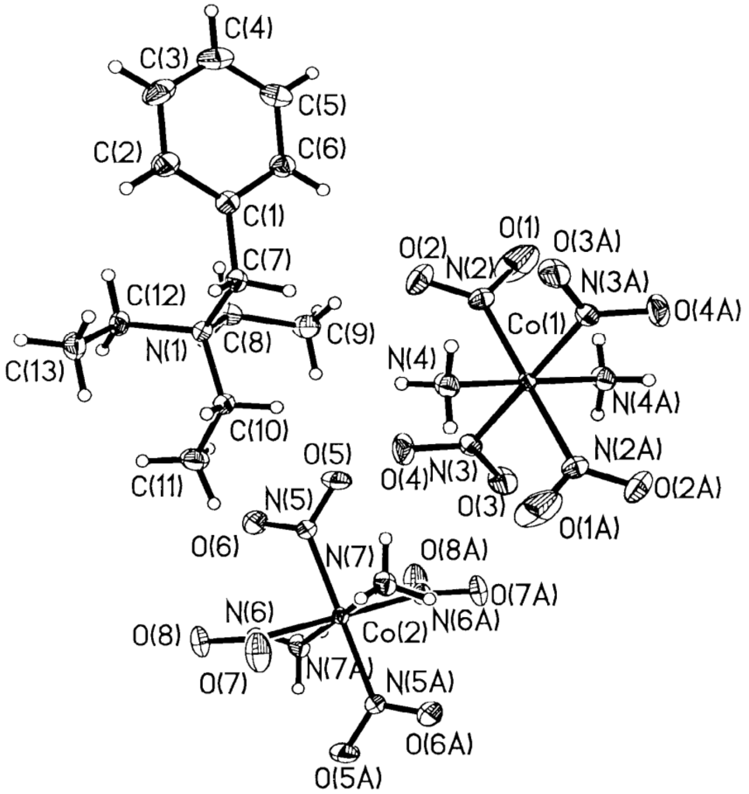


Figure 2. ORTEP diagram of $[(C_2H_5)_3NCH_2C_6H_5][\textit{trans}\text{-}Co(NH_3)_2(NO_2)_4]$ showing the atom numbering scheme.

Table 4. A comparison of selected bond lengths (Å) and angles (°) in $[Co(NH_3)_2(NO_2)_4]^-$ salts containing different cations.

| Compound | Co–$NH_3$ | Co–$NO_2$ | ∠$H_3N$–Co–$NH_3$ | ∠$O_2N$–Co–$NO_2$ | ∠$O_2N$–Co–$NH_3$ | Ref. |
|---|---|---|---|---|---|---|
| **I** | 2.00 | 1.96 | 180.0 | 180.0 | 90.0 | [26] |
| **II** | 2.01 | 1.96 | – | – | – | [17] |
| **III** | 1.94 | 1.95 | 178.7 | 179.1 | 89.9 | [27] |
| **IV** | 1.93 | 1.94 | 180.0 | 180.0 | 90.0 | This work |

$NH_4[\textit{trans}\text{-}Co(NH_3)_2(NO_2)_4]$ (**II**) [19] and $\textit{cis}\text{-}[Co(en)_2(NO_2)_2]\textit{trans}\text{-}[Co(NH_3)_2(NO_2)_4]$ (**III**) [29], as shown in table 4.

The cation consists of three ethyl groups and one benzyl group bonded to nitrogen with the usual tetrahedral geometry. The average C–N bond distance in $[(C_2H_5)_3NCH_2C_6H_5]^+$ is comparable with similar species [28] and is equal to 1.523 Å; the value for $[(CH_3)_4N]^+$ is 1.481 Å [30]. Selected bond angles and lengths are given in table 5; regular geometry is observed. Hydrogen bonding parameters are given in table 6.

Table 5. Selected bond lengths (Å) and angles (°) in $[(C_2H_5)_3NCH_2C_6H_5][trans\text{-}Co(NH_3)_2(NO_2)_4]$.

| | | | |
|---|---|---|---|
| Co(1)–N(4) | 1.933(2) | Co(1)–N(2) | 1.938(2) |
| Co(2)–N(5) | 1.934(2) | Co(1)–N(3) | 1.941(2) |
| Co(2)–N(6) | 1.955(2) | Co(2)–N(7) | 1.926(2) |
| O(1)–N(2) | 1.208(4) | O(2)–N(2) | 1.201(3) |
| O(3)–N(3) | 1.234(3) | O(4)–N(3) | 1.226(3) |
| O(5)–N(5) | 1.227(3) | O(6)–N(5) | 1.222(3) |
| O(7)–N(6) | 1.226(3) | O(8)–N(6) | 1.227(3) |
| N(1)–C(10) | 1.519(4) | N(1)–C(12) | 1.519(3) |
| N(1)–C(8) | 1.523(3) | N(1)–C(7) | 1.533(4) |
| C(1)–C(2) | 1.387(4) | C(1)–C(6) | 1.388(4) |
| C(1)–C(7) | 1.508(4) | C(2)–C(3) | 1.379(5) |
| C(3)–C(4) | 1.383(6) | C(4)–C(5) | 1.374(5) |
| C(5)–C(6) | 1.380(5) | C(8)–C(9) | 1.514(4) |
| C(10)–C(11) | 1.502(5) | C(12)–C(13) | 1.516(4) |
| N(4)–Co(1)–N(3) | 90.26(11) | N(4)–Co(1)–N(2) | 90.14(11) |
| N(2)–Co(1)–N(3) | 92.18(11) | N(7)–Co(2)–N(5) | 90.60(11) |
| N(7)–Co(2)–N(6) | 89.94(11) | N(5)–Co(2)–N(6) | 91.48(10) |
| C(10)–N–C(12) | 111.3(2) | C(10)–N(1)–C(8) | 111.4(2) |
| C(12)–N(1)–C(8) | 106.3(2) | C(10)–N(1)–C(7) | 106.3(2) |
| C(12)–N(1)–C(7) | 111.0(2) | C(8)–N(1)–C(7) | 110.6(2) |
| O(2)–N(2)–O(1) | 117.5(3) | O(2)–N(2)–Co(1) | 122.4(2) |
| O(1)–N(2)–Co(1) | 119.8(2) | O(4)–N(3)–O(3) | 119.3(2) |
| O(4)–N(3)–Co(1) | 120.9(2) | O(3)–N(3)–Co(1) | 119.84(19) |
| O(6)–N(5)–O(5) | 118.4(3) | O(6)–N(5)–Co(2) | 121.4(2) |
| O(5)–N(5)–Co(2) | 120.2(2) | O(7)–N(6)–O(8) | 118.8(3) |
| O(7)–N(6)–Co(2) | 119.8(2) | O(8)–N(6)–Co(2) | 121.4(2) |
| C(2)–C(1)–C(6) | 118.3(3) | C(2)–C(1)–C(7) | 120.6(3) |
| C(6)–C(1)–C(7) | 120.8(3) | C(3)–C(2)–C(1) | 120.9(4) |
| C(2)–C(3)–C(4) | 120.0(4) | C(5)–C(4)–C(3) | 119.8(4) |
| C(4)–C(5)–C(6) | 120.1(4) | C(5)–C(6)–C(1) | 120.9(3) |
| C(1)–C(7)–N(1) | 116.7(2) | C(9)–C(8)–N(1) | 115.1(2) |
| C(11)–C(10)–N(1) | 115.0(3) | C(13)–C(12)–N(1) | 115.8(2) |

Table 6. Hydrogen bonding parameters for $[(C_2H_5)_3NCH_2C_6H_5]$ $[trans\text{-}Co(NH_3)_2(NO_2)_4]$.

| D–H···A | d(D–H) | d(H···A) | ∠DHA | d(D···A) |
|---|---|---|---|---|
| N3–H3A···O1 | 0.890 | 2.194 | 124.00 | 2.791 |
| N3–H3A···O7 | 0.890 | 2.505 | 130.61 | 3.157 |
| N3–H3A···O8 | 0.890 | 2.609 | 115.08 | 3.093 |
| N3–H3C···O3 | 0.890 | 2.174 | 124.66 | 2.778 |
| N6–H6A···O7 | 0.890 | 2.335 | 112.10 | 2.794 |
| N6–H6B···O8[i] | 0.890 | 2.166 | 123.96 | 2.764 |
| N6–H6C···O5[i] | 0.890 | 2.114 | 124.90 | 2.723 |

[i] Equivalent atoms at $-x+1$, $-y$, $-z+1$.

## Acknowledgement

We thank the CSIR, New Delhi, India for their financial support (Grant No. 01(1768)/02/EMR-II).

## References

[1] B. Gruner, J. Plesek, J. Baca, J.F. Dozol, V. Lamare, I. Cisarova, M. Belohradsky, J. Caslarsky, *New J. Chem.* **26**, 887 (2002).

[2] S.A. Dalrymple, M. Parvez, G.K.H. Shimizu, *Inorg. Chem.* **41**, 6986 (2002).

[3] W.G. Jackson, A.F.M.M. Rahman, *Inorg. Chem.* **42**, 383 (2003).
[4] P. Kofod, P. Harris, S. Larsen, *Inorg. Chem.* **42**, 244 (2003).
[5] (a) D.A. Buckingham, L.G. Marzilli, A.M. Sargeson, *J. Am. Chem. Soc.* **89**, 2772 (1967). (b) D.A. Buckingham, J.P. Collman, D.A.R. Happer, L.G. Marzilli, *J. Am. Chem. Soc.* **89**, 1082 (1967).
[6] R.J. Brown, D.A. Buckinghum, C.R. Clark, P.A. Sutton, *Adv. Inorg. Chem.* **49**, 307 (1999).
[7] B.N. Figgis, C.L. Raston, R.P. Sharma, A.H. White, *Aust. J. Chem.* **31**, 2437 (1978).
[8] R.P. Sharma, V. Gupta, K.K. Bhasin, E.R.T. Tiekink, *J. Coord. Chem.* **33**, 117 (1994).
[9] R.P. Sharma, V. Gupta, K.K. Bhasin, M. Quiros, J.M. Salas, *Acta Cryst.* **C50**, 1875 (1994).
[10] R.P. Sharma, K.K. Bhasin, E.R.T. Tiekink, *J. Coord. Chem.* **36**, 225 (1995).
[11] R.P. Sharma, K.K. Bhasin, E.R.T. Tiekink, *Acta Cryst.* **C52**, 2140 (1996).
[12] D.S. Gill, V. Pathania, B.K. Vermani, R.P. Sharma, *Z. Phys. Chem.* **217**, 739 (2003).
[13] R.P. Sharma, R. Sharma, R. Bala, M. Quiros, J.M. Salas, *J. Coord. Chem.* **56**, 1581 (2003).
[14] R.P. Sharma, R. Bala, R. Sharma, K.K. Bhasin, R.K. Chadha, *J. Coord. Chem.* **57**, 313 (2004).
[15] R.P. Sharma, R. Bala, R. Sharma, P. Venugopalan, *J. Mol. Struct.* **694**, 229 (2004).
[16] G. Schlessinger, *Inorg. Synth.* **9**, 110 (1968).
[17] G.M. Sheldrick, *SHELX-97: Program for Solution and Refinement of Crystal Structure Determination*, University of Göttingen, Germany (1997).
[18] P. Hendry, A. Ludi, *Adv. Inorg. Chem.* **35**, 117 (1990).
[19] Y. Komiyama, *Bull. Chem. Soc. Jpn* **30**, 13 (1957).
[20] R. Tsuchida, *Colours and Structures of Metallic Compounds* (1944), p. 96 (as quoted in Ref. [17]).
[21] H. Kuroya, R.T. Suchida, *Bull. Chem. Soc. Jpn* **15**, 427 (1940).
[22] M. Linhard, M. Weiger, *Z. Anorg. Allg. Chem.* **267**, 113 (1950).
[23] I. Nakagawa, T. Shimanouchi, *Spectrochim. Acta.* **23A**, 2099 (1967).
[24] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley and Sons, New York (1997).
[25] R.M. Sieverstein, F.X. Webster, *Spectroscopic Identification of Organic Compounds*, John Wiley and Sons, New York (1998).
[26] H. Karaman, R.J. Barton, B.E. Robertson, D.G. Lee, *J. Org. Chem.* **49**, 4509 (1984).
[27] S. Balt, M.W.G. de Bolster, C. Dekker, *Inorg. Chim. Acta* **17**, 154 (1976).
[28] I. Bernal, *Inorg. Chim. Acta.* **96**, 99 (1985).
[29] I. Bernal, *Inorg. Chim. Acta.* **101**, 175 (1985).
[30] P.D.C. Dietzel, M. Jansen, *Chem. Commun.* 2208 (2001).