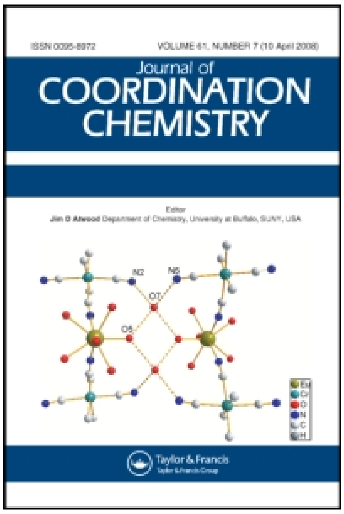

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

A cobalt(III) complex containing coordinated and non-coordinated carboxylates: <i>trans</i>-[(nitro)bis(ethylenediamine)(3,5-dinitrobenzoato)- cobalt(III)][3,5-dinitrobenzoate]

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To cite this Article Sharma, Rajni , Sharma, Raj Pal , Bala, Ritu , Pretto, Loretta and Ferretti, Valeria(2007) 'A cobalt(III) complex containing coordinated and non-coordinated carboxylates: **<i>trans</i>**-[(nitro)bis(ethylenediamine)(3,5-dinitrobenzoato)- cobalt(III)][3,5-dinitrobenzoate]', Journal of Coordination Chemistry, 60: 5, 495 — 504

To link to this Article: DOI: 10.1080/00958970600818468

URL: http://dx.doi.org/10.1080/00958970600818468

Journal of Coordination Chemistry
Vol. 60, No. 5, 10 March 2007, 495–504

Taylor & Francis
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A cobalt(III) complex containing coordinated and non-coordinated carboxylates: *trans*-[(nitro)bis(ethylenediamine)(3,5-dinitrobenzoato)-cobalt(III)][3,5-dinitrobenzoate]

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(*Received in final form 10 March 2006*)

Trans-[(nitro)bis(ethylenediamine)(3,5-dinitrobenzoato)cobalt(III)][3,5-dinitrobenzoate] ([*trans*-$\mathrm{Co(en)_2NO_2(C_7H_3N_2O_6)]C_7H_3N_2O_6}$) has been obtained by mixing aqueous solutions of *trans*-dinitrobis(ethylenediamine)cobalt(III)nitrate and sodium 3,5-dinitrobenzoate in 1 : 1 molar ratio. Elemental analyses and spectroscopic techniques (IR, electronic, ^{1}H and ^{13}C NMR) were used to characterize the complex salt. An X-ray structure determination revealed the salt to consist of discrete [*trans*-$\mathrm{Co(en)_2NO_2(C_7H_3N_2O_6)]^+}$ and $\mathrm{(C_7H_3N_2O_6)^-}$ ions. The salt is triclinic, space group $P\bar{1}$, with $a = 10.3790(1)$, $b = 14.4421(2)$, $c = 14.4421(2)$ Å, $\alpha = 88.0100(4)$, $\beta = 79.1820(4)$, $\gamma = 84.8690(6)^\circ$, $Z = 6$, $V = 3789.50(9)$ Å^3. The crystal lattice is stabilized by electrostatic forces and N–H$\cdots$O hydrogen bonds between cations and anions resulting in a unique salt containing coordinated and non-coordinated 3,5-dinitrobenzoate groups.

Keywords: Cobalt(III); 3,5-Dinitrobenzoate; Spectroscopy; Hydrogen bonding; X-ray structure

1. Introduction

Anions play an important role in chemistry, biology and the environment. It is believed that they participate in 70% of enzymatic reactions [1]. One important class of mono or multiply charged oxyanions is the biologically significant carboxylate series [2]. The carboxylate functions of enzymes, antibodies, amino acids, and metabolic intermediates contribute to their characteristic biochemical behaviour. Also, they can participate through one or more of their carboxylate oxygen atoms in hydrogen-bonding arrays which can control tertiary structure and, consequently, in some cases, function in complex biological molecules. Thus, the design and synthesis of complexing agents for carboxylates has attracted much interest. They differ from tetrahedral oxyanions in many respects; they possess a different geometry and their higher basicity, due to

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ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970600818468

greater charge density on oxygen, is expected to affect cation–anion interactions. The carboxylate ion shows an extraordinary variety in the type of bonding in metal salts and complexes (figure 1) [3, 4]. 3,5-Dinitrobenzoic acid (DNB) contains two nitro groups in addition to the COOH functionality. The presence of additional donor groups can lead to the formation of metal carboxylates with interesting structural features, such as in (triethyleneglycol)bis(3,5-dinitrobenzoate)strontium(II) monohydrate [5], which is a centrosymmetric dimer. One of the DNB ligands behaves as a symmetrical bidentate whereas the other acts as a highly unsymmetrical, tridentate, chelating-cum-bridging ligand.

Hydrogen bonding remains a field of great interest both chemically and biologically. Crystalline complexes of 3,5-dinitrobenzoic acid and 4-methylpyridine were found to be stabilized by very strong hydrogen bonds [6]. We have been studying various reactions of *trans*-dinitrobis(ethylenediamine)cobalt(III) cation [7–9] and have recently reported the structure of *trans*-[nitrobis(ethylenediamine)cobalt(III)(*p*-nitrobenzoato)][*p*-nitrobenzoate *p*-nitrobenzoic acid] [10]. It was expected that a disubstituted carboxylate (3,5-dinitrobenzoate in the present case) would behave in a similar fashion in that the presence of eight N–H hydrogen bond donors on each cation would facilitate interaction with a properly oriented oxoanion. The present study was undertaken to investigate the effect of a disubstituted carboxylate on the reaction type. The synthesis, characterization and X-ray structure packing of *trans*-[(nitro)bis(ethylenediamine)(3,5-dinitrobenzoato)cobalt(III)][3,5-dinitrobenzoate] is presented below.

2. Experimental

2.1. *Materials*

Analytical grade reagents were used without any further purification. [*Trans*-$Co(en_2)(NO_2)_2]NO_3$ was prepared according to a literature method [11].

2.2. *Instruments*

Cobalt was determined by standard method [12]. C, H, N analyses were performed using a Perkin Elmer 2400 system. IR spectrum (KBr pellets) were recorded on a Perkin Elmer Spectrum RX FT-IR instrument. ^1H and ^{13}C NMR were recorded in DMSO-d_6 using a Jeol AL 300 MHz spectrometer with TMS as internal reference.

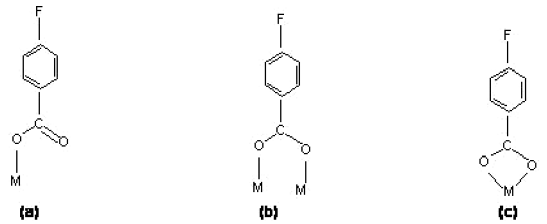

Figure 1. Some common coordination modes in carboxylate group: (a) monodentate; (b) bidentate; (c) bridging.

Electronic spectrum were recorded using an Hitachi 330 spectrophotometer with H_2O as solvent.

2.3. *Synthesis*

Trans-$[Co(en)_2(NO_2)_2]NO_3$ (1 g, 0.003 mol) was dissolved in 50 cm^3 of water and filtered. In another beaker 0.120 g (0.003 mol) of sodium hydroxide and 0.636 g (0.003) of 3,5-dinitrobenzoic acid was dissolved in a minimum of water. Both solutions were mixed slowly at room temperature. The lemon yellow product that appeared immediately was filtered off, washed with water and air-dried (yield 85%). Orange single crystals obtained after one day by recrystallization from hot water were collected by drawing off the mother liquor and air-dried. The salt is stable in air and soluble in water as well as DMSO, but insoluble in acetone. It decomposes at 190°C. Anal. Calcd for [*trans*-$Co(en)_2NO_2(C_7H_3N_2O_6)]C_7H_3N_2O_6$ (%): Co, 9.1; C, 33.3; H, 3.4; N, 19.4. Found: Co, 9.0; C, 33.4; H, 3.4; N, 19.3. Solubility: 0.2 g per 100 mL at 25°C.

2.4. *X-ray crystallography*

Crystal data, data collection and refinement parameters are summarized in table 1 and a selection of bond lengths and angles is reported in table 2. X-ray diffraction data were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å). All intensities were corrected for Lorentz effects, polarization and absorption [13]. The structure was solved by direct methods with SIR97 [14] and refined by full-matrix least-squares using SHELXL-97 [15]. The C1-H_2 fragment belonging to one of the Co1 ethylenediamine ligands is disordered over two equivalent positions. Non-hydrogen atoms were refined anisotropically and

Table 1. Crystal data and structure refinement parameters for [*trans*-$Co(en)_2NO_2(C_7H_3N_2O_6)]C_7H_3N_2O_6$.

Chemical formula	$[(CoN_7O_8C_{11}H_{19})(C_7H_3N_2O_4)]$
M_r	647.38
Cell setting, space group	Triclinic, $P\bar{1}$
a, b, c (Å)	10.3790(1), 14.4421(2), 25.8464(4)
α, β, γ (°)	88.0100(4), 79.1820(4), 84.8690(6)
V (Å^3)	3789.50(9)
Z	6
D_x (Mg m^{-3})	1.702
μ(Mo-Kα) (mm^{-1})	0.77
Crystal form, colour	Plate, Yellow
Crystal size (mm^3)	0.48 × 0.14 × 0.09
Absorption correction	Empirical (SORTAV)
No. of measured, independent and observed parameters	41627, 19229, 11724
Criterion for observed reflections	$I > 2\sigma(I)$
R [$F^2 > 2\sigma(F^2)$], $wR(F^2)$, S	0.054, 0.153, 1.01
No. of relections	19229
No. of parameters	1313
Weighting scheme	Calculated $w = 1/[\sigma^2(F_o^2 + (0.0830P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.66, −0.58

Table 2. Selected bond lengths (Å) and angles (°) for [*trans*-Co(en)$_2$(C$_7$H$_3$N$_2$O$_6$)](C$_7$H$_3$N$_2$O$_6$).

		A	B
Co–N(1)	1.951(3)	1.948(3)	1.939(2)
Co–N(2)	1.942(3)	1.955(3)	1.944(2)
Co–N(3)	1.934(3)	1.950(3)	1.936(3)
Co–N(4)	1.951(3)	1.953(3)	1.943(3)
Co–N(5)	1.898(3)	1.893(3)	1.898(2)
Co–O(3)	1.937(2)	1.927(2)	1.922(2)
O(3)–C(5)	1.286(3)	1.276(4)	1.284(3)
O(4)–C(5)	1.227(4)	1.213(3)	1.222(4)
O(9)–C(12)	1.252(4)	1.243(4)	1.258(4)
O(10)–C(12)	1.230(4)	1.243(4)	1.232(4)
C(12)–C(13)	1.533(4)	1.547(4)	1.538(4)
N(1)–Co–N(2)	86.3(1)	86.1(1)	86.0(1)
N(1)–Co–N(3)	92.5(1)	93.3(1)	94.6(1)
N(1)–Co–N(5)	91.2(1)	91.2(1)	90.8(1)
N(1)–Co–O(3)	86.5(1)	86.9(1)	85.9(1)
N(2)–Co–N(4)	95.0(1)	94.6(1)	93.0(1)
N(2)–Co–N(5)	89.9(1)	90.6(1)	92.9(1)
N(2)–Co–O(3)	91.3(1)	91.0(1)	90.4(1)
N(3)–Co–N(4)	86.1(1)	85.9(1)	86.3(1)
N(3)–Co–N(5)	91.7(1)	85.9(1)	90.2(1)

hydrogen atoms isotropically, with the exception of H atoms belonging to the CH$_2$ groups of the ethylenediamine ligands. These were included at calculated positions, riding on their parent atoms. All other calculations were performed using the programs WinGX [16] and PARST [17]. Hydrogen bonding parameters are reported in table 3.

3. Results and discussion

Trans-dinitrobis(ethylenediamine)cobalt(III) nitrate has played a pivotal role in the development of coordination chemistry. It can react with metal salts of anions in a number of ways depending upon the stoichiometric ratio of reactants. There are few reports of X-ray diffraction studies of dinitrobis(ethylenediamine)cobalt(III) salts in the literature [18–20]. Hydrolysis of *trans*-[Co(en$_2$)(NO$_2$)$_2$]NO$_3$ causes the substitution of one or both nitro groups and leads to *trans*-[Co(en)$_2$(NO$_2$)H$_2$O]$^{2+}$ and *trans*-[Co(en)$_2$(H$_2$O)$_2$]$^{3+}$ [21]. Treatment with solutions containing other anions converts the complexes into *trans*-[Co(en)$_2$X$_2$]$^+$ or *trans*-[Co(en)$_2$(NO$_2$)X]$^+$ [18].

In the present work, *trans*-[Co(en)$_2$(NO$_2$)$_2$]NO$_3$ and sodium 3,5-dinitronitrobenzoate were reacted in a 1 : 1 mol ratio in water with the expectation of similar aquation followed by anation. It should be noted that several reactions have been reported in literature, which involve replacement of a nitro group ligand, such as chloride [22] or oxalatate [23, 24]; the identities of these complexes were confirmed by of single-crystal X-ray studies. The reaction of *trans*-[Co(en)$_2$(NO$_2$)$_2$]NO$_3$ with sodium 3,5-dinitronitrobenzoate results in the formation of the monosubstituted salt, as expected.

Table 3. Hydrogen bonding parameters (Å, °).

D–H···A	D–H	D···A	H···A	∠D–H···A
N1–H43···O9	0.70(4)	2.966(4)	2.52(4)	130(4)
N2–H45···O1A	0.81(4)	2.909(5)	2.19(4)	149(3)
N2–H46···O4	0.92(4)			
N3–H48···O9	0.92(4)	2.849(4)	2.06(4)	143(3)
N4–H49···O4	0.85(4)	2.907(4)	2.16(4)	147(3)
N4–H50···O9B	0.83(4)	2.977(3)	2.35(4)	132(4)
N1A–H51···O1	0.72(4)	2.961(4)	2.32(3)	149(3)
N1A–H52···O10B	0.94(5)	2.979(4)	2.05(5)	166(4)
N2A–H53···O4A	0.78(3)	2.928(3)	2.20(3)	154(3)
N2A–H54···O10A	0.82(4)	2.925(5)	2.22(4)	145(4)
N3A–H56···O9B	0.85(3)	2.988(4)	2.27(3)	142(3)
N4A–H58···O4A	0.90(4)	3.024(4)	2.28(3)	139(3)
N2B–H62···O4B	0.82(4)	2.864(4)	2.17(3)	143(3)
N4B–H65···O4B	0.90(4)	2.988(4)	2.25(4)	139(3)
N3–H47···O2B$^{(i)}$	0.87(4)	2.866(4)	2.13(4)	142(3)
N3B–H63···O7A$^{(ii)}$	0.81(3)	2.893(3)	2.14(3)	154(3)
N4A–H57···O1B$^{(iii)}$	0.80(3)	3.175(5)	2.52(4)	140(3)
	0.89(4)	2.955(4)	2.26(4)	135(4)
N2B–H61···O2$^{(iv)}$	0.94(3)	2.860(4)	2.04(3)	146(3)
N4B–H66···O10$^{(iv)}$	0.82(3)	2.999(3)	2.33(3)	139(3)
N3A–H55···O12A$^{(iv)}$	0.81(3)	3.263(4)	2.73(3)	125(3)
N1B–H59···O2A$^{(v)}$	0.90(3)	2.975(4)	2.22(3)	140(3)
N1B–H60···O9A$^{(v)}$	0.78(3)	2.927(4)	2.19(3)	159(3)
N1–H44···O12$^{(vi)}$	1.02(4)	3.367(4)	2.63(4)	129(3)

Symmetry codes are (i): $x, 1+y, z$; (ii): $-x, -y, 1-z$; (iii): $x+1, y+1, z$; (iv): $x, y-1, z$; (v): $x-1, y-1, z$; (vi): $-x, 1-y, -z$.

3.1. *Spectroscopy*

In IR spectrum, tentative assignments in the region 4000–400 cm^{-1} have been made on the basis of earlier reports in the literature [25]. The band at 785 cm^{-1} is assigned [26] to the CH_2 rocking region and a band at 1596 cm^{-1} is assigned to NH_2 asymmetric deformation. Absorption at 2877 cm^{-1} is due to ring ν(C–H) vibrations and the ν(CO) band appears at 1626 cm^{-1}. The $\nu_a(NO_2)$ band appears at 1458 cm^{-1} and is characteristic of a covalent nitro group [27]; the band at 1326 cm^{-1} is assigned to $\nu_s(NO_2)$ and that at 1421 cm^{-1} to $\nu_a(NO_2)$.

The electronic spectrum of the salt in H_2O in the visible region is identical with that of the complex cation. Maxima at 430 and 337 nm correspond to d–d transitions [28] typical of octahedral low spin cobalt(III) but are shifted due to outer-sphere charge transfer from the free benzoate ion ($^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$, respectively).

In ^{1}H NMR, signals at 4.8 and 6.2 ppm are attributed to protons on the nitrogen atoms of ethylenediamine [29] while CH_2 protons are observed at 2.5 ppm. Signals in the range 9.1–9.5 ppm are attributed to the protons of the benzene ring in the coordination sphere and those at 8.2–8.4 ppm to protons of the benzene ring in the free anion. The peak heights of these signals are consistent with the assignment. ^{13}C NMR spectrum shows a signal at 45 ppm characteristic of carbon atoms of ethylenediamine [30]. The signal at 138 ppm is attributed to carbon atoms of the benzene ring adjacent to the carboxylate group in both cation and anion. The signal at 149.8 ppm is attributed to carbon atoms adjacent to the nitro group. The signals at 130.9 and 124.5 ppm are assigned to other carbon atoms of the benzene ring. Carboxylate carbon atoms show a signal at 190 ppm.

3.2. *Structure description*

An ORTEPIII view of the complex salt is shown in figure 2. The asymmetric unit is constituted of three *trans*-Co(III) cations, each coordinated to two ethylenediamine ligands, a nitro and a 3,5-dinitrobenzoate group (via an oxygen atom), and three 3,5-dinitrobenzoate anions (figure 2). The coordination sphere is almost perfectly octahedral; bond distances and angles in table 2 do not show any significant discrepancy from structural parameters of similar Co complexes. Co–N distances to the ethylenediamine ligands (1.937(2)–1.958(3) Å) are somewhat longer than the Co–N distance to the coordinated NO_2 ion (1.917(2) Å). They compare well to Co–N distances found in *trans*-$[Co(en)_2(NO_2)_2]NO_3$ and those observed in other salts of *trans*-$[Co(en)_2(NO_2)_2]^+$ (table 4). One of the oxygen atoms of the COO^- group of 3,5-dinitrobenzoate bonds to give a strongly asymmetric arrangement of the ligand because of the localization of the double bond; the C5–O3(bound) distances are in the range 1.276(4)–1.286(4) Å, while C5–O4 (free) distances range from 1.213(3) to 1.227(4) Å. These values are compared with a mean value of 1.253 Å for a delocalized carboxylate [23]. In all the three cations the O4 oxygen atom acts as an acceptor in two intramolecular hydrogen bonds (table 3) formed with NH groups of ethylenediamine ligands. In the benzoate anions the symmetry and double bond delocalization of the carboxylate group depends on the strength (and number) of intermolecular hydrogen bonds formed by the two oxygen atoms. Values reported in table 2 show that C12–O9 and C12–O10

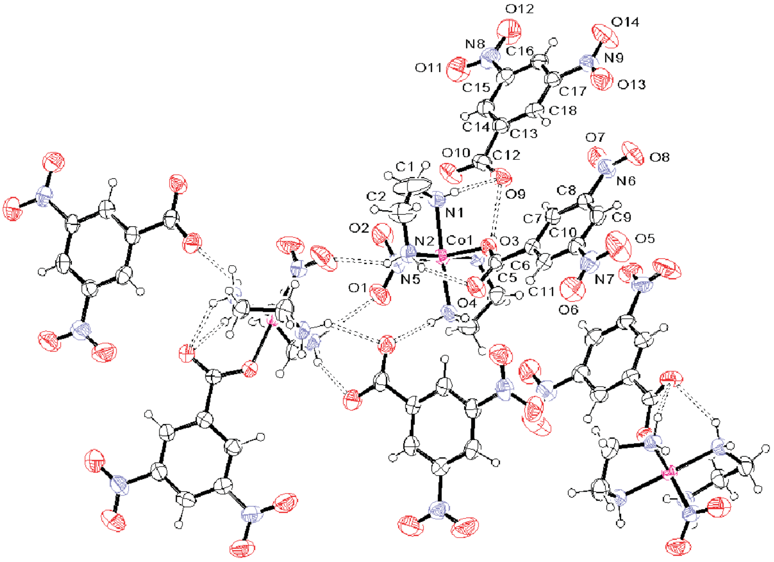

Figure 2. ORTEPIII view of the asymmetric unit. For clarity, the atom numbering of only one cation and one anion is shown. Thermal ellipsoids are drawn at the 40% probability level.

Table 4. A comparison of average bond distances (Å) and bond angles (°) for the cation [*trans*-$Co(en)_2NO_2(C_7H_3N_2O_6)]^+$.

	Bond distances				Bond angles			
Complex salt	Co–N (en)	Co–N (NO_2)	C–N (en)	C–C (en)	N–Co–N	Co–N–C	Co–N–O	Ref.
$[Co(en)_2(NO_2)_2]I$	1.95(1)	1.92(1)	1.49(2)	1.49(3)	87.6(6)	108.6(1)	119.8(1)	[18]
$[Co(en)_2(NO_2)_2]SCN$	1.95(1)	1.92(1)	1.48(1)	1.50(1)	90.0(8)	108.6(2)	121.0(2)	[18]
$[Co(en)_2(NO_2)_2]NO_3$	1.94(2)	1.93(2)	1.47(5)	1.51(5)	89.7(1)	109.7(2)	120.0(2)	[20]
$[Co(en)_2(NO_2)_2]ClO_4$	1.95(5)	1.94(5)	–	–	89.6(2)	–	120.1(4)	[21]
$[Co(en)_2(NO_2)(4\text{-}NO_2C_6H_4CO_2)]^+$ $(4\text{-}NO_2C_6H_4CO_2)\cdot(4\text{-}NO_2C_6H_4CO_2H)^-$	1.94(3)	1.91(3)	1.47(5)	1.50(4)	89.9(12)	109.4(21)	120.0(20)	[10]
$[Co(en)_2NO_2(C_7H_3N_2O_6)]C_7H_3N_2O_6$	1.94(3)	1.89(3)	1.49(4)	1.48(4)	89.4(1)	108.3(4)	120.6(2)	*

*This work.

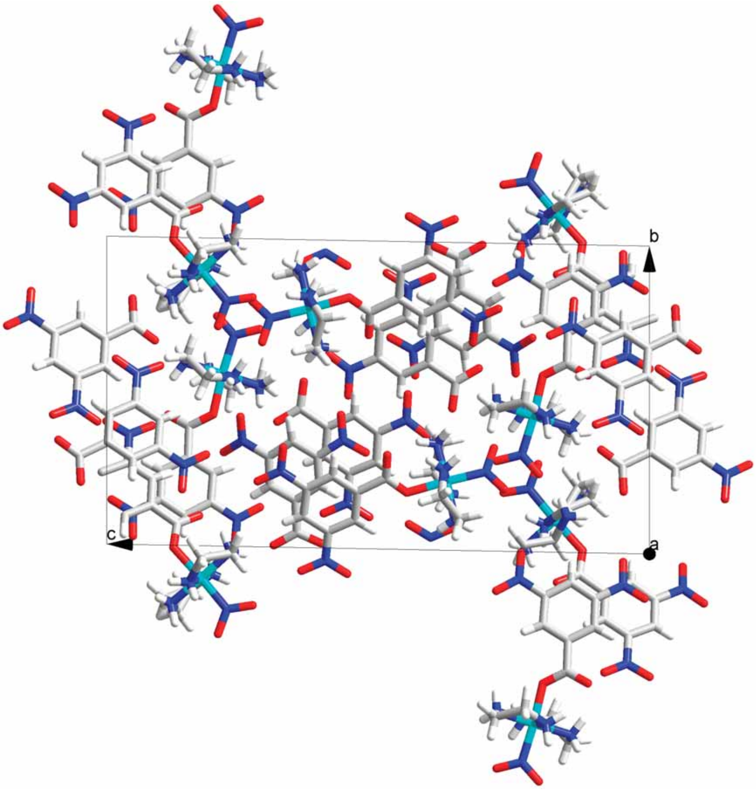

Figure 3. Unit cell packing diagram of the salt viewed along the *a* axis.

distances are similar in only one benzoate anion (A) and O9A and O10A are involved in N1B–H···O9A and N2A–H···O10A hydrogen bonds of comparable strength (N···O distances are 2.927(4) and 2.988(4) Å, respectively). Conversely, in the other two anions the carboxylate group is rather asymmetric, since in both cases the O9 atom (the longer C–O distance) is involved in two N–H···O interactions, while the O10 atom (shorter C–O distance) forms only one N–H···O bond (table 3). The packing architecture is quite complicated and is completely determined by a three-dimensional network of N–H···O hydrogen bonds. The cell contents, viewed along the *a* direction, are shown in figure 3. Bond lengths and bond angles for the coordinated as well as ionic 3,5-dinitrobenzoate ion compare well with those of other 3,5-dinitrobenzoate complexes reported in the literature (table 5) [6, 31, 32].

Supplementary data

Crystallographic data (excluding structure factors) for the structure have been deposited with the Cambridge Crystallographic Data Centre (CCDC 296389). Copies

Table 5. A comparison of average bond distances (Å) and bond angles (°) for the anion $[C_7H_3N_2O_6]^-$.

		Bond distances			Bond angles		
Mode of binding	Compound	C–N	C–O	C–C	O–N–O	O–N–C	Ref.
Ionic	$C_{13}H_{11}N_3O_6$	1.47(2)	1.25(19)	1.50(2)	124.1(15)	117.8(15)	[6]
Ionic	$[Ca(C_6H_{15}NO_3)_2](C_7H_3N_2O_6)_2$	1.48(12)	1.24(10)	1.52(12)	123.6(5)	118.3(8)	[31]
Coordinated	$[Ce(C_7H_3N_2O_6)_6(H_2O)_4]$	1.48(1)	1.25(1)	1.25(3)	126.3(3)	119.1(2)	[32]
Coordinated	$[Co(en)_2NO_2(C_7H_3N_2O_6)]C_7H_3N_2O_6$	1.48(3)	1.25(3)	1.25(3)	125.8(18)	119.0(4)	*
Ionic	$[Co(en)_2NO_2(C_7H_3N_2O_6)]C_7H_3N_2O_6$	1.47(4)	1.24(4)	1.26(4)	124.2(27)	118.7(2)	*

*This work.

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; Email: deposit@ccdc.cam.ac.uk).

Acknowledgments

The authors gratefully acknowledge the financial support of UGC grant F.12-38/2003(SR).

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