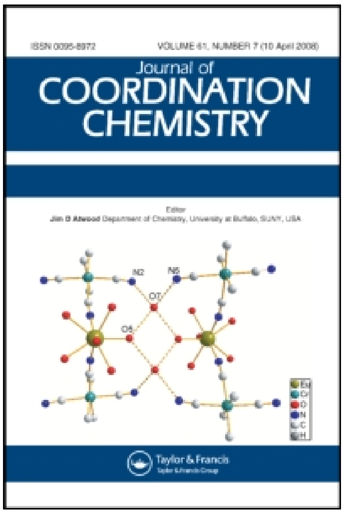

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Synthesis, characterization and X-ray structure of *trans*-[(nitro)bis(ethylenediamine)(*p*-nitrobenzoato) cobalt(III)] [*p*-nitrobenzoate·*p*-nitrobenzoic acid]

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Synthesis, characterization and X-ray structure of *trans*-[(nitro)bis(ethylenediamine)(*p*-nitrobenzoato) cobalt(III)] [*p*-nitrobenzoate·*p*-nitrobenzoic acid]

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The complex salt *trans*-bis(ethylenediamine)dinitrocobalt(III) nitrate reacts with *p*-nitrobenzoic acid in a mixture of water and ethanol to give orange crystals of the novel salt *trans*-[(nitro) bis(ethylenediamine)(*p*-nitrobenzoato)cobalt(III)][*p*-nitrobenzoate · *p*-nitrobenzoic acid], [Co (en)$_2$(NO$_2$)(4-NO$_2$C$_6$H$_4$CO$_2$)][4-NO$_2$C$_6$H$_4$CO$_2$) · 4-NO$_2$C$_6$H$_4$CO$_2$H]. It has been characterized by elemental analysis, spectroscopic techniques and its structure has been determined by single crystal X-ray diffraction methods. The salt is triclinic, space group $P\bar{1}$ with $a = 9.5061(9)$, $b = 9.6367(8)$, $c = 16.2781(14)$ Å, $\alpha = 91.66(1)$, $\beta = 92.91(1)$, $\gamma = 105.03(1)^\circ$, $Z = 2$, $V = 1437.0(2)$ Å^3. The complex consists of *trans*-[Co(en)$_2$NO$_2$(4-NO$_2$C$_6$H$_4$CO$_2$)]$^+$ cations and hydrogen bonded [4-NO$_2$C$_6$H$_4$CO$_2$ · 4-NO$_2$C$_6$H$_4$CO$_2$H]$^-$ anions. The structure is stabilized by additional hydrogen bonds between cations and anions resulting in a unique acid salt containing the cation *trans*-[Co(en)$_2$NO$_2$(4-NO$_2$C$_6$H$_4$CO$_2$)]$^+$.

Keywords: Cobalt(III); 4-Nitrobenzoate; 1,2-Diaminoethane; X-ray structure; Spectroscopy; Hydrogen bonding

1. Introduction

One important class of mono or multiply charged oxyanions concerns carboxylates [1]. The carboxylate function of enzymes, antibodies, amino acids and metabolic intermediates contribute to their characteristic biochemical behaviour. Their involvement in hydrogen bonding can control tertiary structures and consequently in some cases function in biological molecules. They differ from tetrahedral oxyanions in many respects, in particular geometry and basicity, and this too may affect host–guest interactions. Cobalt(III) complexes continue to receive attention [2–6] due to their pivotal role in the development of inorganic chemistry. There are only

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a few reports of X-ray diffraction studies of bis(ethylenediamine)dinitrocobalt(III) salts in the literature [7–9]. Two isomers, *cis* and *trans*, are known [10]. In continuation of the interest in cobalt(III) salts/complexes [11], the synthesis, characterization and single crystal X-ray structure of *trans*-[nitrobis (ethylenediamine)cobalt(III)(*p*-nitrobenzoato)][*p*-nitrobenzoate · *p*-nitrobenzoic acid], *trans*-$[Co(en)_2(NO_2)(4\text{-}NO_2C_6H_4CO_2)][4\text{-}NO_2C_6H_4CO_2 \cdot 4\text{-}NO_2C_6H_4CO_2H]$ is reported in this article.

2. Experimental

Analytical grade reagents were used without any further purification. According to a literature method [10] *trans*-$[Co(en_2)(NO_2)_2]NO_3$ was prepared. Cobalt was determined by a standard method [12]. C, H, N were estimated using a Perkin-Elmer 2400 CHN instrument. IR spectra were recorded with a Perkin-Elmer RX FT-IR spectrophotometer using KBr plates. ^1H and ^{13}C NMR spectra were recorded in dimethylsulphoxide (DMSO-d_6) using a JEOL AL 300 MHz spectrometer. Chemical shifts are given with respect to tetramethylsilane (TMS) as internal standard. Electronic spectra were recorded using a Hitachi 330 spectrophotometer with DMSO as solvent.

2.1. trans-$[Co(en)_2(NO_2)(4\text{-}NO_2C_6H_4CO_2)][4\text{-}NO_2C_6H_4CO_2) \cdot 4\text{-}NO_2C_6H_4CO_2H]$

trans-$[Co(en_2)(NO_2)_2]NO_3$ (1 g, 0.003 mol) was dissolved in 100 cm^3 of water. In another beaker *p*-nitrobenzoic acid (1.0 g, 0.006 mol) was dissolved in 30 cm^3 of ethanol. Both the solutions were mixed and heated at 60–70°C for about 10 min, when reddish brown fumes were evolved. The reaction solution was kept at this temperature for a further 20 min and then cooled to room temperature, when 0.385 g (0.002 mol) of unreacted *p*-nitrobenzoic acid precipitated. This was removed by filtration and the clear filtrate was kept at an ambient temperature. Orange single crystals of *trans*-$[Co(en)_2(NO_2)(4\text{-}NO_2C_6H_4CO_2)][4\text{-}NO_2C_6H_4CO_2 \cdot 4\text{-}NO_2C_6H_4CO_2H]$ were obtained after 2 days; they were collected by decantation and air dried (yield 70%). The salt is sparingly soluble in water, easily soluble in DMSO and insoluble in chloroform. It decomposes at 204°C. Anal. Calcd (%): Co, 8.14; C, 41.40; H, 4.00; N, 15.45. Found: Co, 8.04; C, 41.80; H, 4.82; N, 15.25.

2.2. *Crystallograhy*

Single crystals suitable for X-ray diffraction studies were grown from the mixture of water and ethanol (3 : 1) by slow evaporation. A single crystal of dimensions $0.20 \times 0.20 \times 0.15\,mm^3$ was mounted and used for data collection. Intensity data were collected on a Siemens SMART area-detector diffractometer equipped with a molybdenum tube ($\lambda = 0.71073$ Å) and a highly oriented graphite monochromator. Data were corrected for Lorentz and polarization effects and an empirical absorption correction based on psi scans was applied. The structure was solved by direct methods and refined using SHELX-86 [13]. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods. Details concerning data collection and refinement are summarized in table 1. Atomic coordinates of non-hydrogen atoms

Table 1. Crystal data and structure refinement details for the complex salt.

Empirical formula	$C_{25}H_{29}N_8O_{14}Co$
Formula weight	724.49
Temperature	193(2) K
Radiation used, wavelength	Mo-$K\alpha$, 0.71073 Å
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions	$a = 9.5061(9)$ Å, $\alpha = 1.664(2)^\circ$
	$b = 9.6367(8)$ Å, $\beta = 92.9100(10)^\circ$
	$c = 16.2781(14)$ Å, $\gamma = 105.0290(10)^\circ$
Volume	1437.0(2) Å^3
Z, calculated density	2, 1.674 g cm^{-3}
Absorption coefficient	0.686 mm^{-1}
$F(000)$	748
Crystal size	$0.20 \times 0.20 \times 0.15$ mm^3
Max. and min. transmission	0.695, 0.616
θ range for data collection	1.25 to 29.07°
Index ranges	$-11 \leq h \leq 11, -12 \leq k \leq 11, -21 \leq l \leq 21$
Reflections collected	8456
Independent reflections	4465 ($R_{\text{int}} = 0.0431$)
Refinement method	Full-matrix least-squares on F^2
Data/Restraints/Parameters	4465/0/466
Goodness-of-fit on F^2	0.982
Weighting scheme	$w^{-1} = \sigma^2 F_o^2 + (P)^2 + P$ where $P = (F_o^2 + 2F_c^2)/3$
Data to parameter ratio	
Final R indices [$F > 4\sigma(F)$]	$R_1 = 0.0369$, $wR_2 = 0.0918$
R indices (all data)	$R_1 = 0.0520$, $wR_2 = 0.0974$
Largest diff. peak and hole	0.450 and -0.369 e Å^{-3}

are given in table 2 and the numbering scheme employed is shown in figures 1 and 2. Selected interatomic parameters are given in tables 3 and 4. All hydrogen atoms involved in hydrogen bonding were found in difference Fourier map and were isotropically refined.

3. Results and discussion

Hydrolysis of *trans*-[Co(en$_2$)(NO$_2$)$_2$]NO$_3$ hydrolysis causes the substitution of both nitro groups at the metal centre and leads to *trans*-[Co(en)$_2$(NO$_2$)H$_2$O)]$^{2+}$ and *trans*-[Co(en)$_2$(H$_2$O)$_2$]$^{3+}$ [14]. Treatment with solutions containing other anions converts the complexes into others of the type *trans*-[Co(en)$_2$X$_2$]$^+$ or *trans*-[Co(en)$_2$(NO$_2$)X]$^+$ [7]. In the present case, *trans*-[Co(en)$_2$(NO$_2$)$_2$]NO$_3$ and 4-nitrobenzoic acid were reacted in a 1 : 2 molar ratio in an effort to prepare *trans*-[Co(en)$_2$(4-NO$_2$C$_6$H$_4$CO$_2$)$_2$]NO$_3$, but the possibility of a simple anion exchange yielding *trans*-[Co(en)$_2$(NO$_2$)$_2$](4-NO$_2$C$_6$H$_4$CO$_2$) could not be ruled out. It should be mentioned that several reactions, which involve replacement of a nitro group by chloro or oxalato ligands, have been reported in the literature [15–17]. The identity of these complexes was confirmed by single-crystal X-ray diffraction studies.

In contrast, the reaction of *trans*-[Co(en)$_2$(NO$_2$)$_2$]NO$_3$ with 4-nitrobenzoic acid results in the formation of an orange salt, the analysis of which indicates the presence of three 4-nitrobenzoic acid units. A structure determination by single-crystal X-ray diffraction methods identified the new complex as the acid salt [Co(en)$_2$(NO$_2$)(4-NO$_2$C$_6$H$_4$CO$_2$)][4-NO$_2$C$_6$H$_4$CO$_2$ · 4-NO$_2$C$_6$H$_4$CO$_2$H], containing a cobaltammine cation with nitro and 4-nitrobenzoate groups coordinated to the metal and

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for non H-atoms in the complex salt.

	x/*a*	*y*/*b*	*z*/*c*	*U*(eq)[a]
Co1	9555.4(4)	7065.8(4)	6465.2(2)	19.0(1)
O1	9743(3)	7380(2)	4785.2(12)	44.2(6)
O2	8284(2)	5422(3)	5078.2(12)	38.0(6)
O3	12301.8(19)	8278(2)	7750.6(11)	29.1(5)
O4	9848.6(18)	7539(2)	7632.3(11)	21.5(4)
O5	11829(3)	9631(3)	11908.0(14)	54.0(7)
O6	9743(3)	8063(3)	11831.9(13)	49.1(7)
O7	16767(2)	8285(3)	11829.6(13)	41.6(6)
O8	15001(2)	9329(3)	11738.9(12)	40.0(6)
O9	15215.7(19)	6747(2)	15866.1(11)	29.9(5)
O10	13313(2)	7690(2)	15693.2(12)	34.4(5)
O11	8650(2)	4558(3)	−1031.9(14)	47.4(7)
O12	6479(3)	3915(3)	−1618.2(13)	49.1(7)
O13	5825(2)	3960(2)	2777.5(12)	31.2(5)
O14	3607(2)	2914(3)	2193.5(13)	41.1(6)
N1	10886(3)	5832(3)	6543.3(16)	20.8(5)
N2	8040(3)	5375(3)	6747.3(16)	23.6(6)
N3	11056(2)	8772(3)	6234.5(16)	21.8(5)
N4	8229(3)	8303(3)	6451.2(16)	23.0(6)
N5	9138(2)	6565(3)	5313.9(14)	24.1(6)
N6	10813(3)	8802(3)	11520.6(15)	32.3(6)
N7	15769(3)	8700(3)	12119.9(15)	33.3(6)
N8	7322(3)	4176(3)	−1005.2(16)	32.7(6)
C1	10201(3)	4573(3)	7023.0(17)	25.7(7)
C2	8615(3)	4086(3)	6737.5(18)	27.9(7)
C3	10534(3)	10064(3)	6400.3(18)	25.8(7)
C4	8943(3)	9713(3)	6115.2(18)	27.2(7)
C5	11091(3)	8042(3)	8040.7(16)	20.9(6)
C6	10981(3)	8315(3)	8952.2(16)	20.3(6)
C7	12265(3)	8879(3)	9438.4(17)	25.0(7)
C8	12215(3)	9074(3)	10278.5(17)	26.2(7)
C9	10875(3)	8677(3)	10616.8(16)	24.4(7)
C10	9574(3)	8143(3)	10149.7(17)	24.9(7)
C11	9640(3)	7974(3)	9308.5(17)	24.3(7)
C12	15469(3)	8396(3)	12988.9(17)	26.0(7)
C13	14392(3)	7374(3)	15442.9(17)	24.1(7)
C14	15990(3)	7333(3)	13349.4(17)	29.8(7)
C15	15665(3)	7010(3)	14158.4(17)	27.2(7)
C16	14817(3)	7736(3)	14578.5(16)	21.4(6)
C17	14307(3)	8796(3)	14185.7(17)	27.2(7)
C18	14634(3)	9144(3)	13389.0(18)	29.0(7)
C19	4902(3)	3480(3)	2147.5(17)	27.4(7)
C20	5556(3)	3704(3)	1321.3(17)	24.5(7)
C21	6976(3)	4532(3)	1248.8(17)	25.8(7)
C22	7568(3)	4675(3)	485.9(18)	27.9(7)
C23	6701(3)	4031(3)	−190.1(17)	25.7(7)
C24	5276(3)	3227(3)	−144.5(18)	29.9(7)
C25	4721(3)	3062(3)	632.0(18)	29.0(7)

[a] *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

an acid anion of 4-nitrobenzoic acid. The IR spectrum of the complex was recorded in the region 4000–400 $\text{cm}^{-1}$and tentative assignments have been made on the basis of earlier reports [18]. The band at 795 cm^{-1} is assigned [19] to CH_2 rocking and that at 1576 cm^{-1} to asymmetric NH_2 deformation. The band at 2854 cm^{-1} is due to ring ν(C–H) vibrations; ν(CO) appears at 1634 cm^{-1}. Broad absorption at 3218 cm^{-1} may be assigned to (–OH) groups. The $\nu_a(NO_2)$ band at 1453 cm^{-1} is characteristic of the

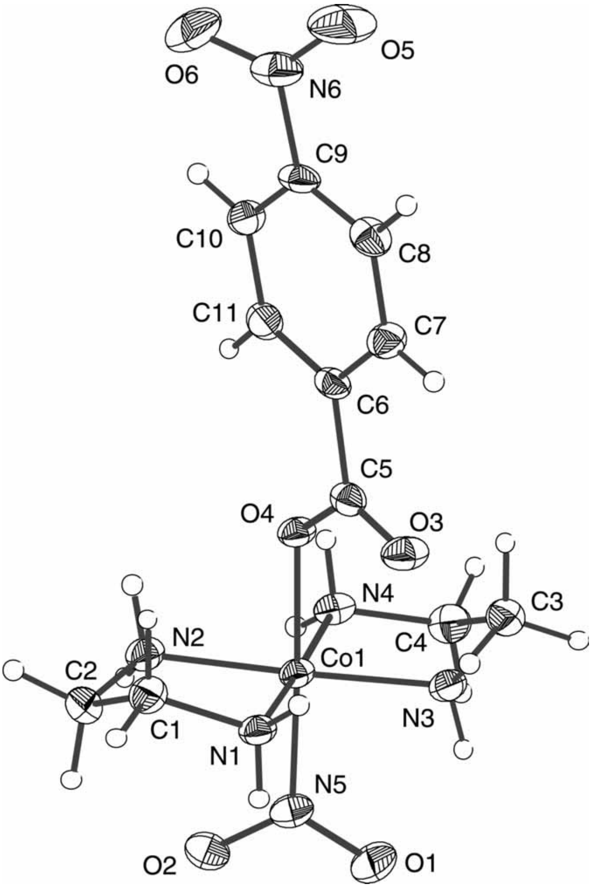

Figure 1. ORTEP view of the structure of the complex cation with the atom numbering scheme. Displacement ellipsoids are shown at the 50% probability level.

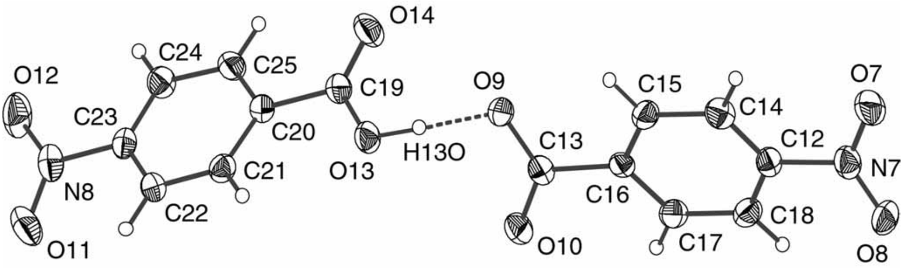

Figure 2. ORTEP view of the structure of the acid anion with the atom numbering scheme. Displacement ellipsoids are shown at the 50% probability level.

covalently bonded nitro group in 4-nitrobenzoate. The band at $1326\,\mathrm{cm}^{-1}$ is assigned to $\nu_s(NO_2)$ and that at $1399\,\mathrm{cm}^{-1}$ to $\nu_a(NO_2)$ of the nitro group coordinated to the metal. The electronic spectrum of the complex salt in DMSO in the visible region is identical with that of the complex cation. Absorption at 468 nm and a shoulder at 259 nm correspond to d–d transitions [20] typical of octahedral, low-spin cobalt(III).

Table 3. Bond lengths (Å) and angles (deg) for the complex cation *trans*-$[Co(en)_2(NO_2)(4\text{-}NO_2C_6H_4CO_2)]^+$ (for numbering scheme see figure 1).

Co1–N5	1.917(2)	N2–C2	1.481(4)
Co1–N3	1.938(2)	N3–C3	1.478(4)
Co1–N1	1.950(2)	N4–C4	1.487(4)
Co1–N4	1.947(2)	N6–C9	1.478(4)
Co1–N2	1.958(2)	C1–C2	1.502(4)
Co1–O4	1.9299(18)	C3–C4	1.507(4)
O1–N5	1.242(3)	C5–C6	1.513(4)
O2–N5	1.225(3)	C6–C11	1.392(4)
O3–C5	1.235(3)	C6–C7	1.394(4)
O4–C5	1.295(3)	C7–C8	1.380(4)
O5–N6	1.215(4)	C8–C9	1.379(4)
O6–N6	1.224(3)	C9–C10	1.388(4)
N1–C1	1.485(3)	C10–C11	1.381(4)
N5–Co1–O4	176.49(8)	O1–N5–Co1	121.0(2)
N5–Co1–N3	91.47(11)	O5–N6–O6	124.1(3)
O4–Co1–N3	91.10(10)	O5–N6–C9	118.0(3)
N5–Co1–N4	91.89(11)	O6–N6–C9	117.9(3)
O4–Co1–N4	85.91(10)	N1–C1–C2	107.6(2)
N3–Co1–N4	86.10(10)	N2–C2–C1	107.2(2)
N5–Co1–N1	91.08(10)	N3–C3–C4	107.7(2)
O4–Co1–N1	91.09(10)	N4–C4–C3	107.0(2)
N3–Co1–N1	94.57(10)	O3–C5–O4	125.7(3)
N4–Co1–N1	176.94(11)	O3–C5–C6	119.8(2)
N5–Co1–N2	90.92(11)	O4–C5–C6	114.5(2)
O4–Co1–N2	86.48(10)	C11–C6–C7	120.3(3)
N3–Co1–N2	177.52(11)	C11–C6–C5	121.3(2)
N4–Co1–N2	93.20(10)	C7–C6–C5	118.4(2)
N1–Co1–N2	86.02(10)	C8–C7–C6	120.1(2)
C5–O4–Co1	126.30(16)	C9–C8–C7	118.3(3)
C1–N1–Co1	108.12(16)	C8–C9–C10	123.1(3)
C2–N2–Co1	110.12(17)	C8–C9–N6	118.9(3)
C3–N3–Co1	109.58(16)	C10–C9–N6	118.0(2)
C4–N4–Co1	110.13(16)	C11–C10–C9	117.9(2)
O2–N5–O1	118.0(2)	C10–C11–C6	120.3(3)
O2–N5–Co1	120.95(18)		

In ^1H NMR, signals at 4.7 and 6.1 ppm are attributed to protons of the nitrogen atoms of ethylenediamine [21] and CH_2 protons are observed at 2.4 ppm. Signals in the range 8.05–8.20 ppm are attributed to the protons of the benzene ring associated with the coordination sphere and those at 7.87–8.01 ppm to protons of the benzene rings in the acid anion; peak heights of these signals are in the ratio 1 : 2. ^{13}C NMR spectra show a signal at 45 ppm characteristic of the carbon atoms of the ethylenediamine ligand. Signals at 148.8 and 148.7 ppm are attributed to carbons of the benzene ring adjacent to the carboxylate groups and the signal at 141.1 ppm is attributed to carbons adjacent to the nitro groups. Signals at 130.3 and 123.1 ppm are assigned to carbons of benzene rings attached to protons and those at 167.5 and 173.6 ppm are assigned to the carboxylate carbon atom of the acid anion and the coordinated ligand, respectively.

The carboxylate ion shows a variety of bonding modes in metal salts and complexes. It can act as a simple counter ion or can coordinate as a monodentate ligand, a bidentate ligand, or can bridge two metal centres. Acid salts, MHX_2, of monocarboxylic acids, HX, can be divided into two classes: (A) $[M(HX_2]$, with the two acidic radicals equivalent and (B) $[MX \cdot HX]$, with the two acid radicals

Table 4. Bond lengths (Å) and angles (deg) for the acid anion $[(4\text{-}NO_2C_6H_4CO_2)\cdot(4\text{-}NO_2C_6H_4CO_2H)]^-$ (for numbering scheme see figure 2).

O11–N8	1.223(3)	O7–N7	1.231(3)
O12–N8	1.225(3)	O8–N7	1.220(3)
O13–C19	1.307(3)	O9–C13	1.291(3)
O14–C19	1.217(3)	O10–C13	1.228(3)
N8–C23	1.475(3)	N7–C12	1.480(3)
C19–C20	1.508(4)	C12–C18	1.376(4)
C20–C25	1.374(4)	C12–C14	1.381(4)
C20–C21	1.391(4)	C13–C16	1.509(4)
C21–C22	1.385(4)	C14–C15	1.394(4)
C22–C23	1.371(4)	C15–C16	1.388(4)
C23–C24	1.381(4)	C16–C17	1.397(4)
C24–C25	1.392(4)	C17–C18	1.380(4)
O11–N8–O12	123.6(2)	O8–N7–O7	124.6(2)
O11–N8–C23	118.2(3)	O8–N7–C12	117.9(2)
O12–N8–C23	118.2(2)	O7–N7–C12	117.5(2)
O14–C19–O13	124.8(3)	C18–C12–C14	123.1(3)
O14–C19–C20	120.6(3)	C18–C12–N7	118.5(3)
O13–C19–C20	114.5(2)	C14–C12–N7	118.4(3)
C25–C20–C21	120.0(3)	O10–C13–O9	124.9(2)
C25–C20–C19	118.6(2)	O10–C13–C16	118.8(2)
C21–C20–C19	121.4(3)	O9–C13–C16	116.2(2)
C22–C21–C20	120.2(3)	C12–C14–C15	118.4(3)
C23–C22–C21	118.2(3)	C16–C15–C14	120.0(3)
C22–C23–C24	123.2(3)	C15–C16–C17	119.4(2)
C22–C23–N8	118.6(3)	C15–C16–C13	121.5(2)
C24–C23–N8	118.2(3)	C17–C16–C13	119.0(2)
C23–C24–C25	117.5(3)	C18–C17–C16	121.4(3)
C20–C25–C24	120.8(3)	C12–C18–C17	117.6(3)

non-equivalent, i.e. X^- and HX can be distinguished in the crystral structure. Infrared spectra of type B compounds are essentially a superimposition of those of the free acids and the neutral salts, while spectra of salts of type A are anomalous. From 4-nitrobenzoic acid an acid potassium salt is readily prepared. However, the failure of repeated attempts to prepare isomorphous ammonium, rubidium, or thallium salts suggests that the structure obtained in the potassium compound depends critically upon the radius of the cation. A structure determination of potassium hydrogen bis(4-nitrobenzoate) [22] revealed that this salt is of type B. It embodies a very short, asymmetric hydrogen bond ($O\cdots O = 2.49$ Å).

Acid salts of nitrophenols have previously been reported [23]. Structures of complexes M(4-np) (where 4-np = 4-nitrophenolate) crystallized together with the parent ligand 4-nitrophenol (4-npH) and with various amounts of water were investigated by single-crystal X-ray diffraction. The 1 : 1 salts $M(4\text{-np})(4\text{-npH})\cdot xH_2O$ are found for all alkali metals M = Li, Na, K, Rb and Cs. Structure determinations have been reported for a number of variously hydrated 4-nitrophenoxide acid salts, $M(4\text{-np})_2\cdot x(4\text{-npH})\cdot yH_2O$, of group 2 elements [24]. $Ca(4\text{-np})_2\cdot 2(4\text{-npH})\cdot 8H_2O$ is monoclinic, $P2_1/n$, $a = 30.52(1)$, $b = 10.02(1)$, $c = 23.65(2)$ Å, $\beta = 116.33(5)°$; $Sr(4\text{-np})_2\cdot 2(4\text{-npH})\cdot 8H_2O$, is monoclinic, $P2_1/c$, $a = 15.57(5)$, $b = 10.08(6)$, $c = 24.20(2)$ Å, $\beta = 117.99(5)°$; $Ba(4\text{-np})_2\cdot 2(4\text{-npH})\cdot 4H_2O$ is orthorhombic, $Fdd2$, $a = 28.01(1)$, $b = 19.90(1)$, $c = 10.69(7)$ Å. Hydrogen bonds between phenoxides of neutral 4-npH and 4-np^- of neighbouring molecule give rise to three-dimensional arrays. All structures define a classical type of acid salt in which the acid is hydrogen bonded to its conjugated base.

In *trans*-[Pb(*p*-$NO_2C_6H_4CO2)_2 \cdot 2H_2O$] [25], reveals, C–O bond lengths are 1.26(7) and 1.29(4) Å and the O–C–O bond angle is 136.0(5)°. The mean C–C bond length in the benzene ring is 1.39(1) Å while the mean C–C–C bond angle is 118.5°. A coordinated water molecule forms an intermolecular hydrogen bond to the oxygen atom of the NO_2 group of the anion ($O_w \cdots NO = 2.4$ Å). Thus discrete molecules of the complex are crosslinked by hydrogen bonds to form a polymeric ribbon along the diagonal of the unit cell. In *trans*-diaquabis(*N*,*N*-diethylnicotinamide-*N*) bis(4-nitrobenzoato-*O*)copper(II) [26], N and O atoms around Cu atom form a square planar arrangement, with slightly tetragonally distorted octahedral coordination completed by two water O atoms at a distance of 2.48(2) Å. H_2O molecules are hydrogen bonded to the carboxyl atom. In [$Co(H_2O)_4$(*p*-$NO_2C_6H_4CO_2)_2] \cdot 2H_2O$ [27], the cobalt atom is situated at a centre of symmetry and is surrounded by six oxygen atoms to form a slightly distorted octahedron. Four positions are occupied by water molecules and the other two by oxygen atoms of the carboxyl groups of 4-nitrobenzoate (the second oxygen atom of these groups is not involved in the coordination). Molecules in the crystal are joined to form a three-dimensional framework by hydrogen bonds between coordinated and lattice water molecules, as well as oxygen atoms of the CO_2^- and NO_2 groups of the anions.

The structure of the present compound was determined unambiguously by single-crystal X-ray diffraction. The crystal consists of *trans*-$[Co(en)_2(NO_2)(4\text{-}NO_2C_6H_4CO_2)]^+$ cations and hydrogen bridged $[(4\text{-}NO_2C_6H_4CO_2) \cdot (4\text{-}NO_2C_6H_4CO_2H)]^-$ anions. In the cation, cobalt is surrounded by five nitrogen atoms of two coordinated ethylenediamine ligands and one nitro group, and one oxygen atom of a 4-nitrobenzoate ligand (figure 1), resulting in octahedral coordination geometry. Compared to the starting dinitro complex, one of the nitro groups in the coordination sphere of the metal has been displaced by 4-nitrobenzoate with retention of *trans* geometry. Co–N distances (ethylenediamine) are in the range 1.937(2) to 1.958(3) Å (table 3), somewhat longer than the distance to the nitrogen atom of the coordinated NO_2 group [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 the *trans*-$[Co(en)_2(NO_2)_2]^+$ cation (table 5). The 4-nitrobenzoate anion acts as a monodentate ligand [Co1–O4 1.930(2) Å] and the C–O distance to the coordinating oxygen atom O4 [1.295(3) Å] is longer than the distance to the non-coordinating O3 atom [1.235(3) Å]. The carboxylic

Table 5. Average bond distances (Å) and angles (deg) of the complex cation in salts $[Co(en)_2(NO_2)_2]X$ (X = I, SCN, NO_3, ClO_4) compared to those of *trans*-$[Co(en)_2(NO_2)(4\text{–}NO_2C_6H_4CO_2)]^+$ (for references see text).

	Bond distances				Bond angles		
Complex salts	Co–N (en)	Co–N (NO_2)	C–N (en)	C–C (en)	N–Co–N	Co–N–C	Co–N–O
$[Co(en)_2(NO_2)_2]I$	1.95(1)	1.92(1)	1.49(2)	1.49(3)	87.6(6)	108.6(1)	119.8(1)
$[Co(en)_2(NO_2)_2]SCN$	1.95(1)	1.92(1)	1.48(1)	1.50(1)	90.0(8)	108.6(2)	121.0(2)
$[Co(en)_2(NO_2)_2]NO_3$	1.94(2)	1.93(2)	1.47(5)	1.51(5)	89.7(1)	109.7(2)	120.0(2)
$[Co(en)_2(NO_2)_2]ClO_4$	1.95(5)	1.94(5)	–	–	89.6(2)	–	120.1(4)
$[Co(en)_2(NO_2)(4\text{-}NO_2C_6H_4CO_2)]^+$ $[(4\text{-}NO_2C_6H_4CO_2) \cdot (4\text{-}NO_2C_6H_4CO_2H)]^-$	1.94(3)	1.91(3)	1.47(5)	1.50(4)	89.9(12)	109.4(21)	12.0(20)[a]

[a] This work.

Table 6. Average bond distances (Å) and bond angles (deg) of the 4-nitrobenzoate moiety in metal salts and complexes (for references see text).

		Bond distances			Bond angles		
Mode of binding	Compound	C–N	C–O	C–C	O–C–O	N–C–C	C–C–C
Coordinated	$[Co(H_2O)_4(4\text{-}NO_2C_6H_4CO_2)_2]\cdot 2H_2O$	1.47(7)	1.39(8)	1.26(7)	124.3(5)	117.9(5)	119.8(5)
Coordinated	$Pb(4\text{-}NO_2C_6H_4CO_2)_2\cdot 2H_2O$	1.49(8)	1.39(8)	1.27(3)	136.0(5)	117.8(4)	118.5(5)
Coordinated	$Cu(4\text{-}NO_2C_6H_4CO_2)_2$ $(C_{10}H_{14}N_2O)_2(H_2O)_2$	1.47(4)		1.25(3)	126.3(3)	119.1(2)	
Coordinated	$[Co(en)_2(NO_2)(4\text{-}NO_2C_6H_4CO_2)]$ $[(4\text{-}NO_2C_6H_4CO_2)\cdot(4\text{-}NO_2C_6H_4CO_2H)]$	1.46(4)	1.38(4)	1.26(3)	125.5(27)	117.5(26)	120.2(27)[a]
Ionic	$[Co(en)_2(NO_2)(4\text{-}NO_2C_6H_4CO_2)]$ $[(4\text{-}NO_2C_6H_4CO_2)\cdot(4\text{-}NO_2C_6H_4CO_2H)]$	1.47(4)	1.38(4)	1.26(4)	124.2(27)	118.7(2)	119.0(28)[a]

[a] This article.

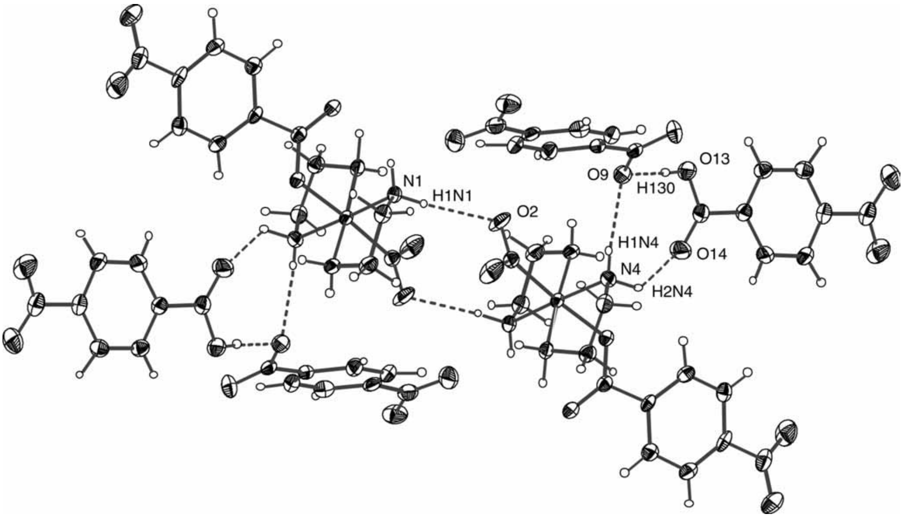

Figure 3. Hydrogen bonding between the acid anion and the complex cation as well as between two complex cations in the crystal of *trans*-[Co(en)$_2$(NO$_2$)(4-NO$_2$C$_6$H$_4$CO$_2$)][4-NO$_2$C$_6$H$_4$CO$_2$ · 4-NO$_2$C$_6$H$_4$CO$_2$H]. Displacement ellipsoids are shown at the 50% probability level.

group and the phenyl ring are practically coplanar [O3–C5–C6–C7 = 2.2(4)°], while the 4-NO$_2$ group is slightly rotated out of this plane [O5–N6–C9–C8 = 22.2(4)°]. The orientation of the coordinated 4-nitro benzoate ligand with respect to the metal fragment is such that the plane of the phenyl ring and the –CO$_2$ group almost bisects the N1–Co1–N3 angle [N1-Co1-O4-C5 = 53.6(2)°].

The acid anion [4-NO$_2$C$_6$H$_4$CO$_2$ · 4-NO$_2$C$_6$H$_4$CO$_2$H]$^-$ is shown in figure 2 and the 4-nitrobenzoate anion and the 4-nitrobenzoic acid molecule are linked together via a strong hydrogen bond [O13–H130 = 0.972(2) Å, O9–H130 = 1.537(2) Å, O9 ··· O13 = 2.506(3) Å, O9–H130–O13 = 173.6(1)°]. Selected bond distances and angles are given in table 4. C–O distances to the oxygen atoms O9 and O13 involved in hydrogen bonding are 1.291(4) and 1.306(3) Å and, as expected, these are longer as compared to those observed to O10 and O14 [1.228(4) and 1.217(3) Å, respectively]. In contrast to the coordinated 4-nitrobenzoate anion, the –CO$_2$ groups in the acid anion are slightly rotated out of the plane of the respective adjacent phenyl rings [O14–C19–C20–C25 = −10.0(4)°, O9–C13–C16–C15 = 22.7(4)°] and the same is observed also for the 4-NO$_2$ groups [O12–N8–C23–C24 = 18.6(4)°, O7–N7–C12–C14 = −18.9(4)°]. Interestingly, in the crystal the two 4-nitrobenzoate units of the acid anion are twisted with respect to each other along the hydrogen bond, thus leading to a conformation in which the planes of the phenyl rings form an angle of about 82°. Other bond lengths and angles for the coordinated 4-nitrobenzoate ligand compare well with those of other 4-nitrobenzoate complexes reported in the literature (table 6). The acid anion interacts with the oxygen atoms O9 and O14 of the carboxyl groups via two more hydrogen bonds to a NH$_2$ moiety (at N4) of the cation (figure 3). In the crystal two such ion pairs are linked together again via hydrogen bonds involving one oxygen atom O2 of the coordinated nitro group and one hydrogen atom of the NH$_2$ group at N1. The resulting units are connected via further hydrogen bonds in the crystal. Hydrogen bonding parameters are given in table 7.

Table 7. Hydrogen bonding parameters for the complex salt (distances in angstroms; angles in degrees).

D–H···A	D–H	H···A	D···A	D–H–A
N1–H1N1···O2^{a}	0.89(3)	2.21(3)	3.094(3)	169(3)
N3–H1N3···O10^{b}	0.85(3)	2.40(3)	2.787(3)	108(2)
O13–H130···O9^{c}	0.972(2)	1.537(2)	2.506(3)	173.6(1)
O13–H130···O10^{c}	0.97(2)	2.54(2)	3.177(3)	122.9(2)
N4–H1N4···O9^{d}	0.84(3)	2.14(3)	2.962(3)	168(3)
N1–H2N1···O10^{b}	0.84(3)	2.59(3)	2.961(3)	108(2)
N1–H2N1···O13^{a}	0.84(3)	2.53(3)	3.217(4)	140(2)
N2–H2N2···O14^{e}	0.87(3)	2.45(3)	3.097(4)	131(3)
N3–H2N3···O10^{b}	0.92(4)	2.45(4)	2.787(3)	102(2)
N4–H2N4···O5^{f}	0.88(3)	2.51(3)	3.296(4)	148(2)
N4–H2N4···O14^{e}	0.88(3)	2.35(3)	2.961(4)	126(2)

Operators for generating equivalent atoms are: (a) $2-x$, $1-y$, $1-z$; (b) x, y, $-1+z$; (c) $2-x$, $1-y$, $2-z$; (d) $-1+x$, y, $-1+z$; (e) $1-x$, $1-y$, $1-z$; (f) $2-x$, $2-y$, $2-z$.

In summary, in *trans*-[Co(en)$_2$(NO$_2$)(4-NO$_2$C$_6$H$_4$CO$_2$)][4-NO$_2$C$_6$H$_4$CO$_2$ · 4-NO$_2$C$_6$H$_4$CO$_2$H] the novel acid anion [4-NO$_2$C$_6$H$_4$CO$_2$ · 4-NO$_2$C$_6$H$_4$CO$_2$H]$^-$ displays a strong hydrogen bond and a twisted orientation. In the crystal both cation and anion participate in extensive hydrogen bonding. This is an uncommon acid salt based on containing *trans*-[Co(en)$_2$NO$_2$(4-NO$_2$C$_6$H$_4$CO$_2$)]$^+$.

Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre (CCDC), CCDC number 244932. 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; email: deposit@ccdc.cam.ac.uk.

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