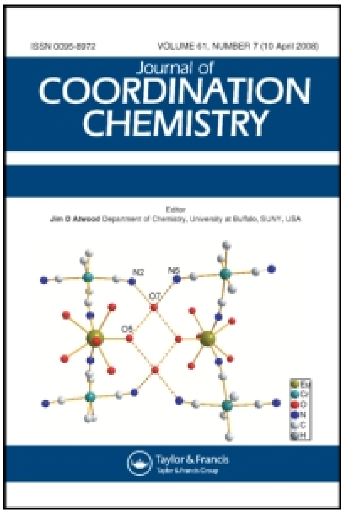

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Synthesis and spectroscopic characterization of *trans*-[Co(en)$_2$(NO$_2$)$_2$]X (X = dodecyl sulfate, picrate, diclofenac or saccharinate) and the single-crystal X-ray structure of the saccharinate salt, *trans*-[Co(en)$_2$(NO$_2$)$_2$](C$_7$H$_4$NSO$_3$)·H$_2$O

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Synthesis and spectroscopic characterization of *trans*-[Co(en)$_2$(NO$_2$)$_2$]X (X = dodecyl sulfate, picrate, diclofenac or saccharinate) and the single-crystal X-ray structure of the saccharinate salt, *trans*-[Co(en)$_2$(NO$_2$)$_2$](C$_7$H$_4$NSO$_3$)·H$_2$O

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trans-[Co(en)$_2$(NO$_2$)$_2$]X complexes, where $X = C_{12}H_{25}SO_4$ (**1**), $C_6H_2N_3O_7$ (**2**), $C_{14}H_{10}Cl_2NO_2$ (**3**) and $C_7H_4NSO_3$ (**4**), have been synthesized by slowly mixing aqueous solutions of *trans*-dinitrobis(ethylenediamine)cobalt(III) nitrate and sodium dodecyl sulfate, picrate, diclofenac and saccharinate, respectively, at a 1 : 1 mol ratio. Good crystals of *trans*-dinitrobis (ethylenediamine)cobalt(III) saccharinate monohydrate, $[Co(en)_2(NO_2)_2](C_7H_4NSO_3)\cdot H_2O$, were obtained. The salt is orthorhombic, space group $P2_12_12$, with $a = 21.553(2)$, $b = 8.503(1)$, $c = 10.238(1)$ Å, $Z = 4$, $V = 1876.3(3)$ Å^3, $R_1 = 0.0286$ and $wR_2 = 0.0727$. A structure determination revealed an ionic structure consisting of discrete $[Co(en)_2(NO_2)_2]^+$ cations and $[C_7H_4SO_3N]^-$ anions.

Keywords: Cobalt(III); Salts; Coordination chemistry; Crystal structure, Spectroscopy

1. Introduction

Anions such as dodecyl sulfate, picrate, diclofenac and saccharinate are industrially and commercially important. Dodecyl sulfate [1] is a useful anionic surfactant. Metal phenolates have a number of applications [2] as antioxidants, surfactants, catalysts, reagents in organic synthesis and as precursors for the preparation of high-temperature superconducting ceramic thin films. The picrate ion shows extraordinary variety in the bonding in metal salts and complexes [3], acting both as a monodentate [4] and a bidentate [5]. Diclofenac is used in nonsteroidal antiinflammatory and analgesic agents [6]. Several of its complexes are more active than the ligand alone [7].

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Saccharin, in the form of its water-soluble salts, is widely used as an artificial sweetener. Saccharin, its derivatives and some metal saccharinates are enzyme inhibitors [8] and find use as electroplating brighteners. The complexes have potential use as antidotes for metal poisoning [9]. Because of the potential carcinogenic nature of saccharin [10], its salts and complexes have been subject to extensive studies. Metal complexes of saccharin may also have relevance to an understanding of its effect on human metabolism [11, 12]. Aside from its biological relevance, its structural versatility in the solid state has proved valuable in several areas of research [13–16].

Cobalt(III) complexes continue to receive attention [17–21] because of their pivotal role in inorganic chemistry. They have application as catalysts in the synthesis and hydrolysis of peptides [22] and are crucial in the vitamin B_{12} system [23]. Cobalt is known for its potent influence on human pathophysiological conditions resulting either from its absence in the body, leading to anemic symptoms [24], or from its excessive presence, leading to toxic effects resulting in heart disease [25]. The role of cobalt(III) complexes in the treatment of biological disorders is well established [26]. There are few reports of structural studies of [bis(ethylenediamine)dinitrocobalt(III)] salts in the literature [27–29], although *cis* and *trans* isomers are known [30]. In continuation [31–39] of our interest in cobalt(III) salts, we report here the synthesis and characterization of *trans*-$[Co(en)_2(NO_2)_2]X$ ($X = C_{12}H_{25}SO_4$, $C_6H_2N_3O_7$ and $C_7H_4NSO_3$) and the single-crystal X-ray structure of the *trans*-[bis(ethylenediamine)dinitrocobalt(III)] saccharinate monohydrate, *trans*-$[Co(en)_2(NO_2)_2](C_7H_4NSO_3) \cdot H_2O$.

2. Experimental

All analytical-grade chemicals and solvents were purchased commercially and used without further purification. Doubly-distilled water was used as solvent. *trans*-$[Co(en_2)(NO_2)_2]NO_3$ was prepared according to a literature method [30].

Cobalt was determined by standard methods [40]. C, H and N were estimated using a Perkin Elmer 2400 CHN instrument. Satisfactory analyses were obtained for all complexes. Noncrystalline samples were dried in a desiccator before analysis. IR spectra were recorded using a Perkin Elmer spectrum RX FTIR system, using Nujol mulls between KBr plates. ^{1}H and ^{13}C NMR spectra were recorded in appropriate deuterated solvents using a Bruker AC 300F (300 MHz) spectrometer with TMS as internal reference. Electronic spectra were recorded using a Hitachi 330 spectrophotometer.

2.1. *trans*-$[Co(en)_2(NO_2)_2](C_{12}H_{25}SO_4)$ (1)

trans-$[Co(en)_2(NO_2)_2]NO_3$ (1 g, 0.003 mol) was dissolved in 50 cm^3 of water and the solution filtered. Sodium dodecyl sulfate (0.861 g, 0.003 mol) dissolved in the minimum amount of water was added to the solution. The lemon yellow product that appeared immediately after mixing was filtered off, washed with water and air-dried (yield 85%).

2.2. *trans*-$[Co(en)_2(NO_2)_2](C_6H_2N_3O_7)$ (2)

trans-$[Co(en)_2(NO_2)_2]NO_3$ (1 g, 0.003 mol) was dissolved in 50 cm^3 of water and mixed together with 0.684 g (0.003 mol) of picric acid in a solution of 0.120 g (0.003 mol) of NaOH dissolved in the minimum amount of water. The yellow product that appeared immediately after mixing was filtered off, washed with water and air-dried (yield 80%).

2.3. *trans*-[Co(en)$_2$(NO$_2$)$_2$]($C_{14}H_{10}Cl_2NO_2$) (3)

trans-[Co(en)$_2$(NO$_2$)$_2$]NO$_3$ (1 g, 0.003 mol) was dissolved in 50 cm^3 of hot water and filtered. To this solution was added 0.9552 g (0.003 mol) of sodium diclofenac dissolved in the minimum amount of water. The light yellow precipitate that appeared within 30 min was filtered off, washed with water and air-dried (yield 70%).

2.4. *trans*-[Co(en)$_2$(NO$_2$)$_2$]($C_7H_4NSO_3$) · H_2O (4)

trans-[Co(en)$_2$(NO$_2$)$_2$]NO$_3$ (1 g, 0.003 mol) was dissolved in 50 cm^3 of water and the solution filtered. To this solution was added 0.6161 g (0.003 mol) of sodium saccharinate dissolved in the minimum amount of water. Yellow crystals appeared after 1 day and these were collected by decantation and air-dried (yield 90%).

Complexes **1**–**4** do not exhibit sharp melting points and decompose at temperatures between 190 and 200°C.

Table 1. Crystal data and structure refinement details for *trans*-[Co(en)$_2$(NO$_2$)$_2$]($C_7H_4NSO_3$) · H_2O.

Empirical formula	$C_{11}H_{22}N_7O_8SCo$
Formula weight	471.35
Temperature	293(2) K
Radiation used, Wavelength	Mo Kα, 0.71073 Å
Crystal system, Space group	Orthorhombic, $P2_12_12$
Unit cell dimensions	$a = 21.553(2)$ Å $b = 8.503(1)$ Å $c = 10.238(1)$ Å
V	1876.3(3) Å^3
Z, Calculated density	4, 1.669 Mg m^{-3}
Absorption coefficient	1.083 mm^{-1}
$F(000)$	976
Crystal size	0.21 × 0.20 × 0.17 mm
Max. and min. transmission	0.830, 0.747
Theta range for data collection	1.89 to 24.99°
Scan type	2θ–θ
Scan speed	2.0 to 60.0° min^{-1} in ω
Index ranges	$-25 \le h \le 0$, $-9 \le k \le 10$, $-10 \le l \le 12$
Reflections collected	1943
Independent reflections	1917 [R(int) = 0.0207]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1917/0/257
Goodness-of-fit on F^2	1.024
Weighting scheme	$1/[\sigma^2(F_o^2) + (0.0342P)^2 + 1.12P]$, $P = [\max(F_o^2,0) + 2F_c^2]/3$
Data to parameter ratio	7.4 : 1
Final R indices, 1735 reflections [$I > 2\sigma(I)$]	$R1 = 0.0286$, $wR2 = 0.0727$
R indices (all data)	$R1 = 0.0329$, $wR2 = 0.0761$
Absolute structure parameter	0.02(2)
Extinction coefficient	0.0085(6)
Largest diff. peak and hole	0.424 and −0.310 e Å^{-3}

Table 2. Final atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for the nonhydrogen atoms of *trans*-$[Co(en)_2(NO_2)_2](C_7H_4NSO_3) \cdot H_2O$.

	x/a	y/b	z/c	U(eq)
Co(1)	10 000	5000	4643(1)	22(1)
Co(2)	10 000	10 000	−387(1)	24(1)
S(1)	8291(1)	8381(1)	2852(1)	34(1)
O(1)	8758(1)	8241(4)	3851(3)	41(1)
O(2)	7914(1)	9777(4)	2962(4)	54(1)
O(3)	8542(1)	6454(5)	−284(3)	58(1)
O(4)	10 427(1)	4377(4)	2134(3)	51(1)
O(5)	9676(1)	5959(4)	7116(3)	43(1)
O(6)	10 242(2)	8914(4)	2120(3)	55(1)
O(7)	9557(2)	9440(4)	−2900(3)	50(1)
O(8)	6605(1)	9800(5)	2843(4)	71(1)
N(1)	8578(2)	8192(5)	1417(3)	41(1)
N(2)	10 000	5000	2741(4)	31(1)
N(3)	10 000	5000	6517(4)	29(1)
N(4)	9096(1)	4952(4)	4643(3)	31(1)
N(5)	9946(2)	2693(3)	4663(3)	27(1)
N(6)	10 000	10 000	1511(4)	32(1)
N(7)	10 000	10 000	−2291(4)	33(1)
N(8)	10 045(2)	12 308(3)	−387(3)	31(1)
N(9)	9105(1)	10 290(4)	−431(4)	34(1)
C(1)	7825(2)	6670(5)	2826(4)	33(1)
C(2)	7919(2)	5960(5)	1636(4)	36(1)
C(3)	7612(2)	4571(6)	1339(5)	52(1)
C(4)	7213(2)	3948(7)	2246(6)	65(2)
C(5)	7127(2)	4671(6)	3446(6)	58(2)
C(6)	7435(2)	6043(6)	3763(4)	46(1)
C(7)	8373(2)	6865(6)	817(4)	40(1)
C(8)	8883(2)	3381(5)	4216(4)	41(1)
C(9)	9292(2)	2212(5)	4910(4)	36(1)
C(10)	9430(2)	12 974(6)	−668(6)	57(1)
C(11)	8936(2)	11 949(6)	−265(8)	75(2)

2.5. *Structure determination*

Yellow, single crystals of *trans*-$[Co(en)_2(NO_2)_2](C_7H_4NSO_3) \cdot H_2O$ (**4**) suitable for X-ray diffraction studies were grown from aqueous solution by slow evaporation. A single crystal of dimensions 0.21 × 0.20 × 0.17 mm was mounted along the longest dimension and used for data collection. Intensity data were collected on a Siemens P4 single-crystal diffractometer equipped with a sealed molybdenum tube ($\lambda = 0.71073$ Å) and a highly oriented graphite monochromator. Lattice parameters were obtained by a least-squares fit to 40 reflections. Data were collected by the 2θ–θ scan mode with variable scan speeds ranging from 2.0 to $60.0^\circ \text{min}^{-1}$. Data were corrected for Lorentz and polarization effects and an empirical absorption correction based on the psi scans method was applied. An extinction correction was applied. All other relevant information concerning data collection and refinement is given in table 1. The structure was solved by direct methods and refined using the SHELX-97 package of programs [41]. Atomic coordinates for the nonhydrogen atoms are given in table 2 and hydrogen-bonding parameters in table 3.

Crystallographic data (excluding structure factors) for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 237636. Copies of the data can be obtained free of charge on

Table 3. Hydrogen bonding parameters for [*trans*-Co(en)$_2$(NO$_2$)$_2$](C$_7$H$_4$NSO$_3$) · H$_2$O.

D–H	*d*(D–H)	*d*(H···A)	$\angle$DHA	*d*(D···A)	A
O8–H8E	0.924	1.951	156.91	2.824	O2
O8–H8F	0.892	2.137	160.00	2.991	O3^{i}
N4–H4A	0.900	2.142	156.19	2.987	O8^{ii}
N4–H4A	0.900	2.410	118.85	2.951	O5
N4–H4B	0.900	2.220	144.98	3.001	O1
N5–H5A	0.900	2.196	143.42	2.968	O6^{iii}
N5–H5A	0.900	2.562	112.43	3.022	O1^{iii}
N5–H5B	0.900	2.397	113.66	2.879	O5^{iii}
N8–H8A	0.900	2.386	111.11	2.837	O6^{iv}
N8–H8B	0.900	2.275	138.82	3.012	O5^{v}
N8–H8B	0.900	2.641	111.99	3.093	O7^{iv}
N9–H9A	0.900	2.212	122.90	2.805	O7
N9–H9A	0.900	2.212	122.90	2.805	O7

Symmetry transformations used: $^{i}\,-x+3/2,\ y+1/2,\ -z$; $^{ii}\,-x+3/2,\ y-1/2,\ -z+1$; $^{iii}\,-x+2,\ -y+1,\ z$; $^{iv}\,-x+2,\ -y+2,\ z$; $^{v}\,-x+2,\ -y+2,\ z-1$.

Table 4. Characteristic IR (cm^{-1}) and electronic spectroscopic data for the salts.

	δ(CH$_2$)	δ(NH$_2$)	ν_{as}(NO$_2$)	ν_{as}(CO)	ν(CN)	ν(SO$_2$)	ν(SO$_3$)	(λ_{max}/nm)
1	890	1598	1463				1059	434, 342
2	889	1590	1461	1641				438, 348
3	890	1572		1548				440, 356
4	790	1573		1633	1334	1136		434, 347

application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

3. Results and discussion

3.1. *Spectroscopic properties*

Characteristic IR data for the salts are given in table 4. IR assignments were made on the basis of earlier reports [42]. The IR band in the range 790–890 cm^{-1} is assigned to CH$_2$ rocking and the band in the range 1572–1598 cm^{-1} is assigned to NH$_2$ asymmetric deformation [43] of ethylenediamine. One peak in each region confirms the *trans* geometry of the cation. Bands at 1059 and 1463 cm^{-1} are assigned to ν(SO$_3$) and ν_{as}(NO$_2$) in **1**. Bands at 3120, 1870 and 1488 cm^{-1} are assigned to ν(C–H), ν(C–C) and ν(C–O) and a band at 1461 cm^{-1} is assigned to ν_{as}(NO$_2$) in **2**. These values are in good agreement with the literature values for the picrate ion. In **3**, the band at 1441 is assigned to ν(C–C). The band at 1548 is assigned to ν_{as}(C–O) and that at 1452 cm^{-1} to ν_{s}(C–O). Some of the important peaks of ionic saccharinate in the IR spectra of **4** were assigned by comparison to related compounds [44]. The peak at 2854 cm^{-1} is due to ring ν(C–H) vibrations and the ν(CO) peak appears at 1633 cm^{-1}. The peak at 1334 cm^{-1} is due to ν(CN) and ν_{as}(SO$_2$) appears as a strong peak at 1246 cm^{-1} while ν_{s}(SO$_2$) appears as a strong peak at 1136 cm^{-1}. The band at 1283 cm^{-1} is assigned to aromatic ring ν[C–C]. Weak bands in the region 430–450 cm^{-1} are due to Co–N stretching.

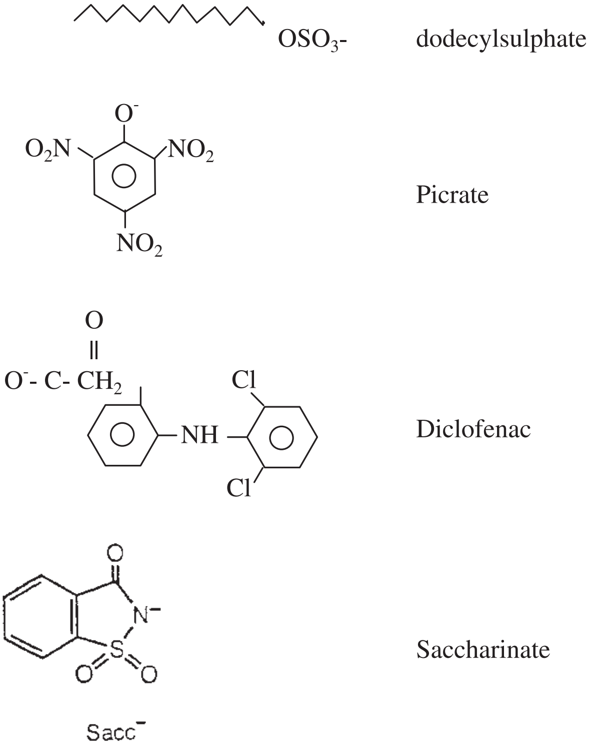

Figure 1. Anions present in the complex salts.

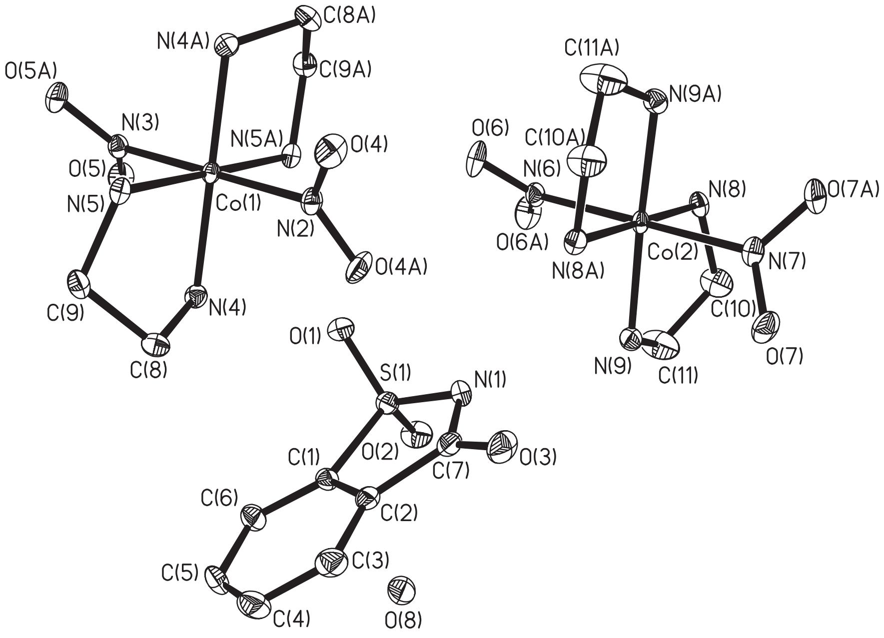

Figure 2. ORTEP diagram of *trans*-$[Co(en)_2(NO_2)_2]_2(C_7H_4NSO_3) \cdot H_2O$ showing the atom labeling scheme.

Table 5. Selected bond lengths [Å] and angles [°] for **4**.

Co(1)–N(3)	1.919(4)	Co(1)–N(2)	1.947(4)
Co(1)–N(4)	1.950(3)	Co(1)–N(5)	1.965(3)
Co(2)–N(6)	1.943(4)	Co(2)–N(9)	1.946(3)
Co(2)–N(7)	1.950(5)	Co(2)–N(8)	1.965(3)
S(1)–O(1)	1.440(3)	S(1)–O(2)	1.442(3)
S(1)–N(1)	1.602(4)	S(1)–C(1)	1.768(4)
O(3)–C(7)	1.235(5)	O(4)–N(2)	1.230(3)
O(5)–N(3)	1.236(4)	O(6)–N(6)	1.230(4)
O(7)–N(7)	1.236(4)	N(1)–C(7)	1.358(6)
N(4)–C(8)	1.479(5)	N(5)–C(9)	1.488(5)
N(8)–C(10)	1.471(6)	N(9)–C(11)	1.467(6)
C(1)–C(2)	1.375(6)	C(1)–C(6)	1.382(6)
C(2)–C(3)	1.387(6)	C(2)–C(7)	1.500(6)
C(3)–C(4)	1.373(7)	C(4)–C(5)	1.386(8)
C(5)–C(6)	1.381(7)	C(8)–C(9)	1.507(6)
C(10)–C(11)	1.435(7)		
N(3)–Co(1)–N(2)	180.0	N(3)–Co(1)–N(4)	90.02(9)
N(2)–Co(1)–N(4)	89.98(9)	N(2)–Co(1)–N(5)	90.58(9)
N(3)–Co(1)–N(5)	89.42(9)	N(4)–Co(1)–N(5)	85.39(15)
N(6)–Co(2)–N(9)	91.32(11)	N(9)–Co(2)–N(8)	85.55(15)
N(6)–Co(2)–N(7)	180.0	N(9)–Co(2)–N(7)	88.68(11)
N(6)–Co(2)–N(8)	90.00(9)	N(7)–Co(2)–N(8)	90.00(9)
O(1)–S(1)–O(2)	113.9(2)	O(1)–S(1)–N(1)	111.95(17)
O(2)–S(1)–N(1)	111.8(2)	O(1)–S(1)–C(1)	109.83(19)
O(2)–S(1)–C(1)	111.01(17)	N(1)–S(1)–C(1)	97.1(2)
C(7)–N(1)–S(1)	111.9(3)	C(2)–C(1)–C(6)	122.4(4)
C(2)–C(1)–S(1)	106.9(3)	C(6)–C(1)–S(1)	130.8(4)
C(1)–C(2)–C(3)	119.8(4)	C(1)–C(2)–C(7)	111.5(4)
C(3)–C(2)–C(7)	128.7(4)	C(4)–C(3)–C(2)	118.6(5)
C(3)–C(4)–C(5)	120.8(5)	C(6)–C(5)–C(4)	121.2(5)
C(5)–C(6)–C(1)	117.1(5)	O(3)–C(7)–N(1)	123.5(4)
O(3)–C(7)–C(2)	123.8(5)	N(1)–C(7)–C(2)	112.7(4)
N(4)–C(8)–C(9)	106.0(3)	N(5)–C(9)–C(8)	107.0(3)
C(11)–C(10)–N(8)	112.2(4)	C(10)–C(11)–N(9)	111.6(4)

Absorption maxima for the salts are listed in table 4. Electronic spectra were recorded in DMSO. Strong absorption bands at around 440 and 350 nm correspond to d–d transitions typical of octahedral low-spin cobalt(III) [45], from the $^1A_{1g}$ ground state to $^1T_{1g}$ (lower energy) and $^1T_{2g}$ (higher energy). The data show that all salts contain the *trans*-[Co(en)$_2$(NO$_2$)$_2$]$^+$ ion.

The anions present in the complex salts are shown in figure 1. In ^{1}H NMR spectra, the two signals at around 4.5 and 4.9 ppm are attributed to nitrogen protons of ethylenediamine, while CH$_2$ protons of the ethylenediamine [46] group are observed at around 2.4 ppm in all complexes (^{13}C NMR spectra show a characteristic signal at 45 ppm for carbons of ethylenediamine). In **1**, signals at 1.5, 1.2 and 0.69 ppm are attributed to protons of carbons 1 and 2, carbons 3–11 and carbon 12, respectively. The carbon attached to oxygen of the sulfate group is numbered 1. In the ^{13}C NMR spectrum, carbon 1 appears at 65.0 ppm. The signal at 29.0 ppm is attributed to carbons 2 and 4–9. Carbon 3 appears at 26.1 ppm and carbons 10, 11 and 12 appear at 32.0, 23.0 and 14.1, respectively. In **2**, the ^{1}H NMR signal at 7.7 ppm is attributed to protons of the benzene ring. In ^{13}C NMR, the two carbons next to the carbon adjacent to the phenoxy group appear at 138.0 ppm. Two signals at 124.9 and 124.8 ppm are attributed to carbons adjacent to the *p*-nitro group and adjacent carbons next to this carbon. The carbon adjacent to the phenoxy group appears at 160.1 ppm.

Table 6. Comparison of bond distances [Å] and angles [°] for *trans*-$[Co(en)_2(NO_2)_2]^+$ and the saccharinate ion.

Cation	Co–N1	Co–N2	C–N	C–C	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)			27
$[Co(en)_2(NO_2)_2]SCN$	1.95(1)	1.92(1)	1.48(1)	1.50(1)	90.0(8)	108.6(2)	121.0(2)			27
$[Co(en)_2(NO_2)_2]NO_3$	1.94(2)	1.93(2)	1.47(5)	1.51(5)	89.7(1)	109.7(2)	120.0(2)			29
$[Co(en)_2(NO_2)_2]ClO_4$	1.95(5)	1.94(5)			89.6(2)		120.1(4)			28
$[Co(en)_2(NO_2)_2]C_7H_4NSO_3$	1.95(3)	1.93(4)	1.35(6)	1.39(6)	89.6(6)	109.3(2)	120.0(3)			A
Anion	**C–S**	**S–O**	**S–N**	**C–N**	**C–O**	**∠CSO**	**∠CSN**	**∠OSN**	**∠OSO**	**Ref.**
$C_7H_5NSO_3$	1.42		1.66	1.37	1.21		92.4		117.5	8
$NaC_7H_4NSO_3$	1.44(2)				1.23(3)				112.9(1)	54
$KC_7H_4NSO_3$	1.44(3)				1.22(5)				112.4(2)	54
$NH_4C_7H_4NSO_3$	1.45(1)				1.24(2)				113.4(1)	54
$[Co(en)_2(NO_2)_2]C_7H_4SO_3N \cdot H_2O$	1.76(4)	1.44(3)	1.60(4)	1.35(6)	1.23(5)	110.4(18)	97.1(2)	111.8(9)	113.9(2)	A
$SO_3C_7H_4NSn(C_6H_5)3 \cdot C_2H_5OH$	1.77(8)	1.42(9)	1.63(8)	1.37(9)	1.25(1)	113.0(5)	94.8(4)	110.9(4)	116.1(4)	55
$C_{10}N_4COPb(C_7H_4NSO_3)_2 \cdot H_2O$	1.75(16)	1.48(12)	1.61(13)	1.30(19)	1.23(20)	112.1(8)	96.8(7)	112.1(7)	116.1(7)	56

N1 = nitrogen of ethylenediamine, N2 = nitrogen of nitrite, A = this work.

In **3**, the ^{1}H NMR signal at 6.9 ppm is attributed to N*H* and aromatic protons are observed between 6.3 and 7.5 ppm. The signal at 3.9 ppm is attributed to the CH$_2$ group attached to the ring. In ^{13}C NMR, the carboxylate carbon appears at 142.7, the carbon of the –CH$_2$ group attached to the ring at 137.0, and aromatic carbons in the range 115.9–130.0 ppm. In the saccharinate salt **4**, a signal at 7.7 ppm (^{1}H NMR) is assigned to protons of the aromatic region. In ^{13}C NMR, signals at 145.9, 119.5, 123.6, 131.6, 132.1, 134.1 and 166.6 ppm are assigned to C1 to C7 of the saccharinate ion, respectively [47].

3.2. *X-ray crystallography*

The deprotonated forms of saccharin show extraordinary variety in type of bonding in metal salts and complexes, being ionic [48, 49], coordinated as a monodentate through nitrogen [50], the carbonyl oxygen atom [51] or the sulfonyl oxygen atom [52], or a bridging bidentate [53]. Several modes may occur in a single structure. Spectroscopic studies showed that in **4** the saccharinate ion is not coordinated, as confirmed by the structure analysis.

An ORTEP diagram of the structure of **4** (figure 2) shows that the salt consists of [Co(en)$_2$(NO$_2$)$_2$]$^+$ cations and saccharinate anions. Selected bond distances and angles are given in table 5. Bond lengths and bond angles of the anion in **4** are comparable with those of other ionic saccharinates (table 6), which means there is no cation dependence. This is best illustrated by a comparison of data for **4** and NaC$_7$H$_4$NSO$_3$. In **4**, S–O = 1.44(3) Å, C–O = 1.23(5) Å and ∠O–S–O = 113.9(2)° and in NaC$_7$H$_4$NSO$_3$, S–O = 1.44(2) Å, C–O = 1.23(3) Å and ∠O–S–O = 112.9(1)°. Average C–N and C–C bond distances in the cation differ slightly from those in other salts containing *trans*-[Co(en)$_2$(NO$_2$)$_2$]$^+$ (table 6), but other bond distances and angles are comparable with those in the literature. The structure of the salt **4** is stabilized by electrostatic forces of attraction and hydrogen-bonding interactions (table 3).

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