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A comparative study of the interactions of cobalt(III) with naphtholate and phenolate moieties

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The structural motif of piperidinium bis[*N*-(2-hydroxynaphthalen-1-yl)sarcosinato]cobaltate(III), $(C_5H_{10}NH_2)[Co(C_{14}H_{13}NO_3)_2]$, (I), displays a chain of two alternating discrete mononuclear Co^{III} complex anions with intervening piperidinium counter-ions. The piperidinium cations and complex anions interact *via* N—H···O hydrogen bonding. Each of the tridentate ligands coordinates to the Co atom in a facial mode, giving a pseudo-octahedral geometry consistent with the mixed donor-atom environment, and each complex anion exhibits C_i symmetry about the metal centre. The average $Co^{III}—O_{naphtholate}$ distance in (I) lies within the observed range of normal values for $Co^{III}—O_{phenolate}$ distances in related compounds, indicative of similarity of coordination behaviour between the naphtholate and phenolate moieties.

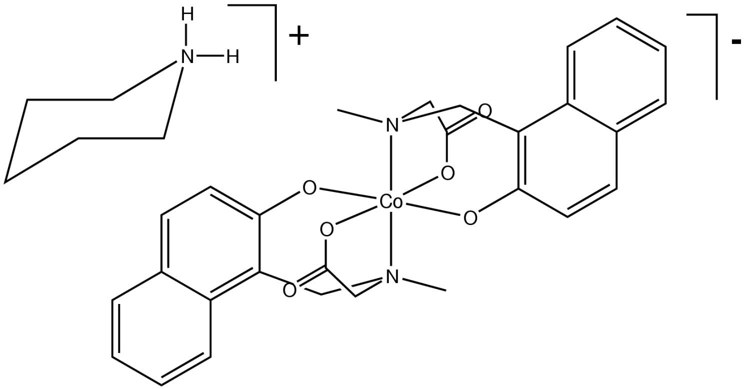
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.044
wR factor = 0.102
Data-to-parameter ratio = 18.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Curiously, crystallographic elucidation of cobalt(III)–naphtholate interactions is an extremely rare occurrence, despite the ease and strength with which the naphtholate O-atom donor coordinates to the Co^{III} ion. Up until now, only two structurally characterized naphtholate-containing complexes of cobalt(III) have been reported (Kurahashi, 1976; Xiaojie *et al.*, 1986). In contrast, the literature has witnessed a steady increase in the number of structural accounts of complexes of Co^{III} possessing a phenolate moiety. Naphtholates are closely related to phenolates electronically, as amply illustrated by the similarity of the colours of their transition metal complexes relative to those of the corresponding complexes with phenolates, but unlike phenolates, naphtholates do not exist at biosites of metallobiomolecules. Hence, naphtholates have received very little attention in coordination chemistry over the years. In our quest to compare and contrast the basicities and donor abilities of the naphtholate and phenolate O atoms, we have synthesized the title compound, $(C_5H_{10}NH_2)[CoL_2]$,



(I)

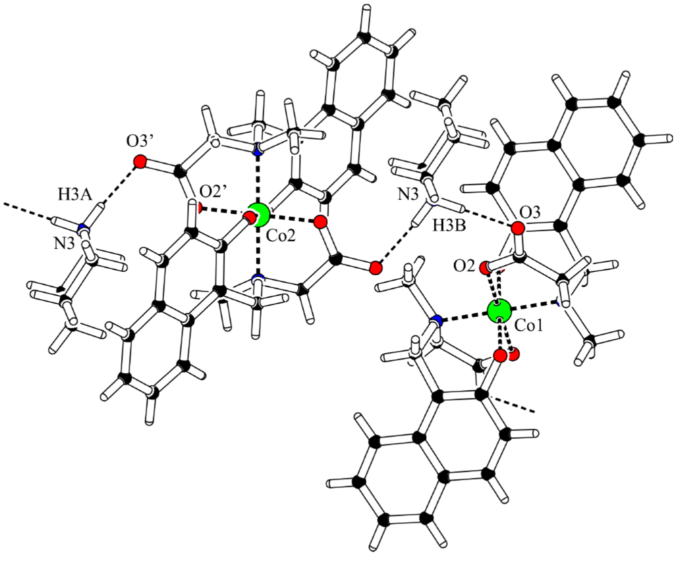


Figure 1
Interactions of the piperidinium cations with the complex anions through hydrogen bonding.

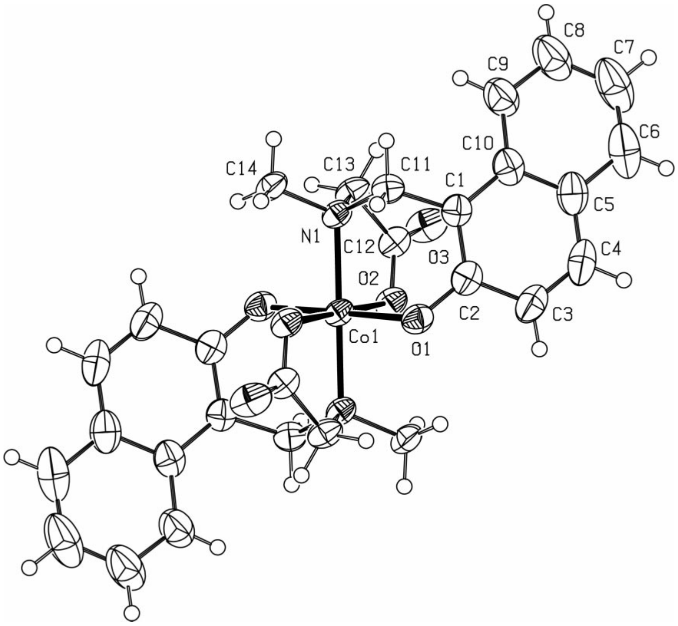


Figure 2
View of one of the two complex anions of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

(I) [H_2L = *N*-(2-hydroxynaphthalen-1-yl)sarcosine], and characterized it by single-crystal X-ray analysis, several spectroscopic techniques and cyclic voltammetry. Co^{III} ($S = 0$) is an ideal transition metal ion for the study of the coordination behaviour of the naphtholate moiety, given that its electronic structure does not tamper with the coordination sphere.

Compound (I) was synthesized by reaction of the ligand H_2L with Co^{II} in the presence of piperidine as base and atmospheric oxygen as oxidant. The crystal structure of (I) has revealed the existence of two similar, but not identical, discrete cobalt(III) complex anions in the unit cell linked *via* a piperidinium cation, $[C_5H_{10}NH_2]^+$, through intermolecular hydrogen bonding involving the carbonyl O atoms of the complex anions (Fig. 1 and Table 2). The two complex anions alternate around the piperidinium cation to form a hydrogen-bonded chain. As expected, the piperidinium ion adopts the chair conformation. Each complex anion consists of two tridentate *N*-(2-hydroxynaphthalen-1-yl)sarcosinate ligands related by a crystallographically imposed centre of inversion (Fig. 2). In accord with the mixed-donor set, the geometry at the metal centre is distorted octahedral with the donor atoms (naphtholate oxygen, tertiary amine nitrogen and carboxylate oxygen) arranged facially around the cobalt ion. The monodentate coordination of the carboxylate group is consistent with the solid-state IR spectroscopic data [$\nu(C{=}O) - \nu(C{-}O) = 225\ cm^{-1}$] (Nakamoto, 1997).

The structure of (I) resembles that of the analogous manganese(III) compound, the only difference being that the complex anions of the latter compound exhibited Jahn–Teller distortion (Shongwe *et al.*, 2001). Selected bond distances and angles for the complex anions in (I) are given in Table 1.

The bond distances $Co^{III}{-}O_{naphtholate}$ [1.9076 (17)–1.9139 (17) Å], $Co^{III}{-}N_{amine}$ [1.9915 (18)–1.9922 (18) Å] and $Co^{III}{-}O_{carboxylate}$ [1.9033 (16)–1.9120 (15) Å] compare favourably with the values observed in related complexes, such as $[Co(tan)_2]ClO_4$ [Htan = 1-(2-thiazolylazo)-2-naphthol; $Co^{III}{-}O_{naphtholate}$ = 1.886 (4)–1.889 (4) Å] (Kurahashi, 1976), $[CoL]CO_2Me$ [H_2L = *N*,*N*′-(3,3′-dipropylamine)bis(salicylideneamine); $Co^{III}{-}N_{amine}$ = 1.983 (9) Å] (Matsumoto *et al.*, 1983), and $[Co(NH_3)_6][CoL_2]_2Cl$ [H_2L = *o*-hydroxybenzylglycine; $Co^{III}{-}O_{carboxylate}$ = 1.907 (2)–1.913 (2) Å] (Chen *et al.*, 1991). Evidently, the $Co^{III}{-}O_{naphtholate}$ distance is indistinguishable from those of $Co^{III}{-}O_{phenolate}$ [normal range: 1.862 (6) Å (Nassimbeni *et al.*, 1976) to 1.928 (2) Å (Chen *et al.*, 1991)]. Clearly, the donor properties of the naphtholate and phenolate moieties are comparable.

Experimental

Compound (I) was synthesized by reaction of the ligand *N*-(2-hydroxynaphthalen-1-yl)sarcosine (Wilson, 1990) with half the amount of Co^{II} ions in the presence of piperidine. To a suspension of the ligand (0.098 g, 0.40 mmol) in methanol (10 ml) was added piperidine (0.068 g, 0.80 mmol), and the mixture was stirred until a clear colourless solution was obtained. Then $CoBr_2$ (0.044 g, 0.20 mmol) was added, whereupon a yellow colour developed immediately. On further stirring (15 min) under ambient conditions, the colour of the solution darkened progressively, finally becoming red–brown. The solution was filtered and allowed to stand overnight during which time red–orange blocks of crystals of (I) were deposited. The supernatant was decanted and the crystals were washed with cold ethanol followed by diethyl ether and then dried *in vacuo* over P_4O_{10}. Yield: 0.069 g (55%). Elemental analysis: found (%) C 62.53, H 6.08, N 6.38; calculated (%) C 62.75, H 6.06, N 6.65.

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Crystal data

$(C_5H_{12}N)[Co(C_{14}H_{13}NO_3)_2]$	$Z = 2$
$M_r = 631.59$	$D_x = 1.388$ Mg m^{-3}
Triclinic, $P\overline{1}$	Mo $K\alpha$ radiation
$a = 10.130$ (2) Å	Cell parameters from 965 reflections
$b = 11.778$ (2) Å	$\theta = 2.5$–25.8°
$c = 13.065$ (3) Å	$\mu = 0.62$ mm^{-1}
$\alpha = 99.608$ (4)°	$T = 293$ (2) K
$\beta = 90.336$ (5)°	Plate, dark red
$\gamma = 100.351$ (4)°	$0.18 \times 0.18 \times 0.02$ mm
$V = 1510.8$ (5) Å^3	

Data collection

Bruker SMART 1K CCD diffractometer	7345 independent reflections
ω scans	4286 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$R_{\rm int} = 0.028$
$T_{\rm min} = 0.866$, $T_{\rm max} = 0.988$	$\theta_{\rm max} = 28.3^\circ$
10784 measured reflections	$h = -13 \rightarrow 10$
	$k = -15 \rightarrow 15$
	$l = -13 \rightarrow 17$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.044$	$w = 1/[\sigma^2(F_o^2) + (0.0433P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.102$	$(\Delta/\sigma)_{\rm max} < 0.001$
$S = 0.93$	$\Delta\rho_{\rm max} = 0.23$ e Å^{-3}
7345 reflections	$\Delta\rho_{\rm min} = -0.35$ e Å^{-3}
392 parameters	

Table 1
Selected geometric parameters (Å, °).

Co1—O2	1.9033 (16)	Co2—O1′	1.9076 (17)
Co1—O1	1.9139 (17)	Co2—O2′	1.9120 (15)
Co1—N1	1.9915 (18)	Co2—N1′	1.9922 (18)
O2—Co1—O1	90.86 (7)	O1′—Co2—O2′	90.42 (7)
O2—Co1—N1	86.43 (7)	O1′—Co2—N1′	93.34 (8)
O1—Co1—N1	93.33 (7)	O2′—Co2—N1′	84.10 (7)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N3—H3A⋯O3′$^{\rm i}$	0.90	1.85	2.743 (3)	169
N3—H3B⋯O3$^{\rm ii}$	0.90	1.83	2.728 (3)	175

Symmetry codes: (i) $1 - x, -y, -z$; (ii) $x - 1, y, z$.

H atoms were located from difference Fourier maps, and were positioned geometrically and allowed to ride on their parent atoms.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 1999); program(s) used to refine structure: *SHELXTL*; molecular graphics: *PLATON* (Spek, 1990); software used to prepare material for publication: *SHELXTL*.

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