METAL-ORGANIC COMPOUNDS

Sodium Dinitritobis(pyrazine-2-carboxyl-ato-*N*,*O*)cobaltate(III)

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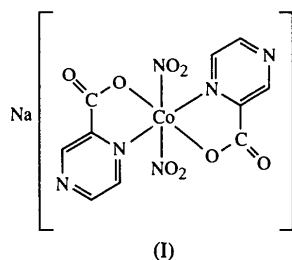
Fig. 1. The molecular structure of the [Co(pyrazine-2-carboxylate)$_2$-(NO$_2$)$_2$]$^-$ anion showing 50% probability displacement ellipsoids (*ORTEP*II; Johnson, 1976).

Abstract

The Co atom within the centrosymmetric anion in Na[Co(C$_5$H$_3$N$_2$O$_2$)$_2$(NO$_2$)$_2$] is chelated *via* an O atom [Co—O 1.889 (1) Å] and the adjacent pyrazine N atom [Co—N 1.899 (2) Å] of two pyrazine-2-carboxylate ligands, as well as *via* the N atom of two nitrite anions [Co—N 1.954 (2) Å].

Comment

When a solution of pyrazine-2-carboxylic acid in ethanol was added to an aqueous solution of sodium cobalt nitrite in a 3:1 molar ratio, both orange (major product) and yellow crystals were obtained from the reddish violet solution which resulted. The yellow product corresponds to [Co(pyrazine-2-carboxyl-ate)$_2$(OH$_2$)$_2$], which has been characterized previously (O'Connor & Sinn, 1981), and the structure determination of the orange crystals, (I), is reported herein.

(I)

The complex anion (Fig. 1) is situated about a centre of inversion and the Co atom is chelated by two pyrazine-2-carboxylate anions. Coordination occurs *via* one of the carboxylate O atoms and the N atom adjacent to this group leading to the formation of a five-membered ring. The octahedral geometry is completed by two N-bound nitrate anions; the distortion from ideal geometry is minimal. The Co—O and Co—N bond distances of 1.889 (1) and 1.899 (2) Å, respectively, are shorter, as expected, than the corresponding distances of 2.093 (1) and 2.102 (2) Å found in the structure
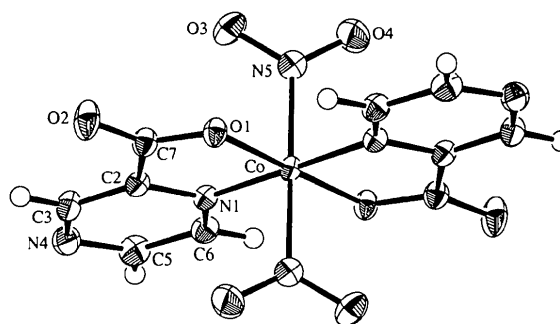
of [Co(pyrazine-2-carboxylate)$_2$(OH$_2$)$_2$] (O'Connor & Sinn, 1981) which features a Co^{II} centre.

The Na cation, located on a centre of symmetry, exists in a distorted octahedral N$_2$O$_4$ environment, defined by the remaining N [2.594 (2) Å] and O [2.379 (1) Å] atoms of the carboxylate ligands and a pair of O(3) atoms [2.403 (1) Å] derived from the nitrite groups. The non-coordination of the O(4) atom is reflected in the disparate N—O bond distances of 1.251 (2) and 1.220 (2) Å found in the nitrite groups.

Experimental

The addition of a solution of pyrazine-2-carboxylic acid in ethanol to an aqueous solution of sodium cobalt nitrite in a 3:1 molar ratio gave a reddish violet solution with evolution of NO$_2$ gas. When left to stand overnight, both orange (major product) and yellow crystals deposited from the solution. The yellow product corresponds to [Co(pyrazine-2-carboxyl-ate)$_2$(OH$_2$)$_2$].

Crystal data

Na[Co(C$_5$H$_3$N$_2$O$_2$)$_2$(NO$_2$)$_2$]	Mo *K*α radiation
M_r = 420.12	λ = 0.7107 Å
Triclinic	Cell parameters from 25
$P\bar{1}$	reflections
a = 7.238 (2) Å	θ = 4.0–12.0°
b = 8.881 (2) Å	μ = 1.336 mm^{-1}
c = 6.140 (1) Å	T = 293.2 K
α = 99.81 (2)°	Plate
β = 112.84 (2)°	0.34 × 0.19 × 0.03 mm
γ = 99.81 (2)°	Orange
V = 346.0 (1) Å^3	
Z = 1	
D_x = 2.016 Mg m^{-3}	

Data collection

Rigaku AFC-6*R* diffractom-eter	1596 observed reflections
$\omega/2\theta$ scans	R_{int} = 0.0302
	θ_{max} = 27.5°

Absorption correction:
  refined from ΔF
  (*DIFABS*; Walker &
  Stuart, 1983)
  $T_{min} = 0.974$, $T_{max} = 1.000$
1723 measured reflections
1596 independent reflections

$h = 0 \rightarrow 9$
$k = -11 \rightarrow 11$
$l = -7 \rightarrow 7$
3 standard reflections
  monitored every 400
  reflections
  intensity decay: 3%

Refinement

Refinement on F
$R = 0.0339$
$wR = 0.0283$
$S = 1.791$
1596 reflections
121 parameters
H-atom parameters not
  refined

Weighting scheme based
  on measured e.s.d.'s;
  $w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.0015$
$\Delta\rho_{max} = 0.41$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}
Atomic scattering factors
  from *International Tables
  for X-ray Crystallography*
  (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Co	0	0	0	0.01702 (9)
Na	0	1/2	1/2	0.0261 (3)
O(1)	−0.0076 (2)	0.1272 (1)	−0.2189 (2)	0.0216 (3)
O(2)	0.1741 (2)	0.3488 (2)	−0.2415 (3)	0.0356 (4)
O(3)	−0.0965 (2)	0.2744 (2)	0.1629 (3)	0.0335 (4)
O(4)	−0.2798 (3)	0.0656 (2)	0.1866 (3)	0.0377 (5)
N(1)	0.2578 (2)	0.1464 (2)	0.2184 (3)	0.0188 (4)
N(4)	0.6354 (3)	0.3716 (2)	0.4624 (3)	0.0265 (4)
N(5)	−0.1442 (3)	0.1279 (2)	0.1347 (3)	0.0235 (4)
C(2)	0.3133 (3)	0.2565 (2)	0.1140 (3)	0.0203 (5)
C(3)	0.5022 (3)	0.3670 (2)	0.2374 (4)	0.0251 (5)
C(5)	0.5744 (3)	0.2656 (2)	0.5667 (4)	0.0262 (5)
C(6)	0.3851 (3)	0.1509 (2)	0.4467 (3)	0.0229 (5)
C(7)	0.1504 (3)	0.2469 (2)	−0.1361 (3)	0.0221 (5)

Table 2. *Selected geometric parameters* (Å, °)

Co—O(1)	1.889 (1)	N(1)—C(2)	1.344 (2)
Co—N(1)	1.899 (2)	N(1)—C(6)	1.335 (2)
Co—N(5)	1.954 (2)	N(4)—C(3)	1.331 (3)
O(1)—C(7)	1.283 (2)	N(4)—C(5)	1.332 (3)
O(2)—C(7)	1.225 (2)	C(2)—C(3)	1.376 (3)
O(3)—N(5)	1.251 (2)	C(2)—C(7)	1.507 (3)
O(4)—N(5)	1.220 (2)	C(5)—C(6)	1.394 (3)
O(1)—Co—N(1)	85.85 (6)	O(3)—N(5)—O(4)	120.9 (2)
O(1)—Co—N(5)	89.77 (6)	N(1)—C(2)—C(3)	120.2 (2)
N(1)—Co—N(5)	89.84 (7)	N(1)—C(2)—C(7)	113.9 (2)
Co—O(1)—C(7)	114.3 (1)	C(3)—C(2)—C(7)	125.8 (2)
Co—N(1)—C(2)	111.5 (1)	N(4)—C(3)—C(2)	122.4 (2)
Co—N(1)—C(6)	129.7 (1)	N(4)—C(5)—C(6)	122.7 (2)
C(2)—N(1)—C(6)	118.8 (2)	N(1)—C(6)—C(5)	119.3 (2)
C(3)—N(4)—C(5)	116.5 (2)	O(1)—C(7)—O(2)	125.6 (2)
Co—N(5)—O(3)	118.6 (1)	O(1)—C(7)—C(2)	114.1 (2)
Co—N(5)—O(4)	120.6 (1)	O(2)—C(7)—C(2)	120.3 (2)

The values of T obtained from *DIFABS* (Walker & Stuart, 1983) have been normalized by multiplying them by $1/T(m)$, where $T(m)$ was the maximum value of T obtained by the program. It is recognized that the range of T values thus obtained may not be as great as might be expected from crystals of this shape.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduc-

tion: *TEXSAN* (Molecular Structure Corporation, 1992). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1045). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Benzyltrichloro(1,10-phenanthroline-*N*,*N'*)-tin(IV) Benzene Solvate (1/1)

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Abstract

The octahedral Sn atom in the title complex, [SnCl₃(C₇H₇)(C₁₂H₈N₂)].C₆H₆, is coordinated by one C, three Cl and two N atoms such that the two N atoms occupy positions *trans* to two of the Cl atoms, leaving one Cl atom *trans* to the C atom. This has the result that there are two classes of Sn—Cl interaction.

Comment

The Sn atom in [BzSnCl₃(phen)], (I), where Bz is benzyl and phen is 1,10-phenanthroline, exists in a distorted octahedral geometry defined by a C atom of the benzyl group, three Cl atoms and the two N atoms of a chelating 1,10-phenanthroline ligand. The greatest