

Poly[methylammonium tris(μ_2 -formato- κ^2 O:O')cobalt(II)]Miroslav Boča,^{a,b,*} Ingrid Svoboda,^b Franz Renz^c and Hartmut Fuess^b

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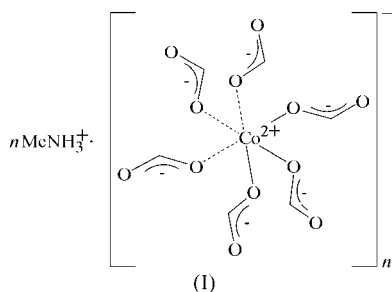
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The structure of the title compound, $\{(\text{CH}_6\text{N})[\text{Co}(\text{CHO}_2)_3]\}_n$, consists of a three-dimensional net of central Co^{II} ions connected *via* formate (methanediolate) bridges. The negative charge is compensated by protonated methylamine cations. The CoO_6 chromophores form slightly distorted octahedra, which are bridged by C atoms of formate groups. The central Co atom lies on an inversion center and most of the other atoms lie on an *m* plane.

Comment

The initial aim of the present study was the preparation of single crystals of cobalt(II) complexes containing ligands with a Schiff base group and pyridine *N*-oxide fragments, in order to compare these complexes with known copper(II), zinc(II) and iron(III) complexes (Boča, Baran *et al.*, 2000). During the recrystallization of the starting complex from methylformamide, decomposition of the complex occurred. The mechanism of this decomposition seems to be complicated.



The following factors can play an important role: (i) the presence of water in the starting complex; (ii) the presence of a pyridine *N*-oxide fragment and its basic properties; (iii) the basic nature of methylformamide; (iv) the acid properties of the remaining part of the ligand. Taking into account all these acid–base properties, the following processes can be expected:

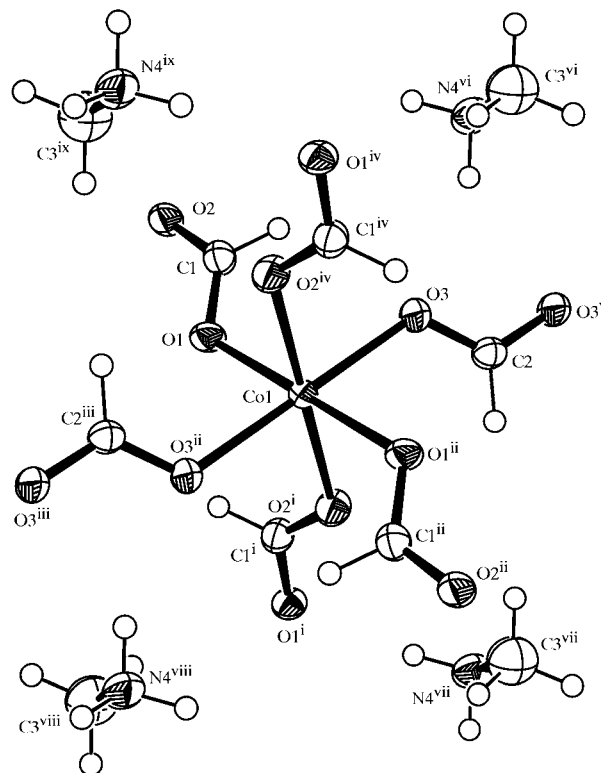


Figure 1

The structure and atom-numbering of the title compound, showing 50% probability displacement ellipsoids. H atoms are shown as circles of arbitrary radii. [Symmetry codes: (i) $-x + \frac{1}{2}, -y, z + \frac{1}{2}$; (ii) $-x, -y, -z$; (iii) $-x, y + \frac{1}{2}, -z$; (iv) $x + \frac{1}{2}, y, -z + \frac{1}{2}$; (v) $x, -y + \frac{1}{2}, z$; (vi) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{1}{2}$; (vii) $x - \frac{1}{2}, -y + \frac{1}{2}, -z - \frac{1}{2}$; (viii) $-x + \frac{1}{2}, -y + 1, z - \frac{1}{2}$; (ix) $-x + \frac{1}{2}, -y + 1, z + \frac{1}{2}$.]

(i) decomposition of the ligand into the starting compounds; (ii) evolution of oxygen from the pyridine *N*-oxide fragment; (iii) evolution of methylamine from methylformamide; (iv) protonation of methylamine; (v) formation of the formyl group. The Co atom is probably involved in some of these processes, which result in the formation of the title compound, (I). The evolution of methylamine from methylformamide is mentioned in the literature in basic environments of Co^{III} systems (Angus *et al.*, 1993).

The structure of (I) consists of a three-dimensional net of central Co^{II} ions connected *via* formate (methanediolate, CHOO^-) bridges. The negative charge is compensated by protonated methylamine cations, CH_3NH_3^+ . The electro-neutral fragment surrounding the Co atom is shown in Fig. 1. The central Co atom lies on an inversion center and most of the other atoms lie on an *m* plane. The CoO_6 chromophores form slightly distorted octahedra, which are bridged by C atoms of formate groups. Selected bond distances and angles are shown in Table 1. All three O–Co–O axes are perfectly linear, forming angles of 180° . However, these axes are not perpendicular to one another. Three different Co–O bond distances are observed, in the range characteristic of Co^{II} –O coordination bonds. The closest $\text{Co}\cdots\text{Co}$ distance is 5.840 (1) Å, which is half the length of the diagonal of the *ac* plane. The second shortest $\text{Co}\cdots\text{Co}$ contact is only slightly

longer, at 5.855 (1) Å, which is half the length of the *b* axis. In addition, the C–O bond lengths in the formate group are normal, as are the values of the O–C–O angles for the bridging functionality. Three classical N–H···O hydrogen bonds are present (Table 2 and Fig. 2), and two C–H···O hydrogen-bond contacts were also detected (not shown).

The Cambridge Structural Database (CSD; Allen, 2002) contains 19 more examples of a formate group coordinated to Co^{II} ions. The coordination behavior of the formate group varies considerably. In some cases, it behaves as a bidentate ligand coordinated by both O atoms to the same central Co^{II} ion [CSD refcodes NABHAZ (Sernau, Huttner & Walter, 1996) and NABHAZ01 (Sernau, Huttner, Scherer & Walter, 1996)]; in other cases, the formate group behaves as a bridging species between Co atoms [OXCFOR (Cornils *et al.*, 1976), ABOLOS (Saalfrank *et al.*, 2001), COKCIO (Clegg & Sykes, 1984) and UFIQEF (Cadiou *et al.*, 2002)] or between one Co atom and one other central metal atom (MOTQER; Arici *et al.*, 2002). Structures with chain motifs are also well documented. Chains containing only central Co atoms [COFORM01 (Kaufman *et al.*, 1993), COFORM10 (Antsyshkina *et al.*, 1967), PAKNIY (Fujino *et al.*, 1992), PAKNIY01, PAKNIY10, PAKNIY11 and YAMKOM (Ridwan, 1992), DEJLEJ (Rettig *et al.*, 1999), and DEJLEJ01 and CADFOD (Domasevitch *et al.*, 2002)] and chains containing both central Co and Cu atoms [XIHDEX (Leyva *et al.*, 2001) and OLEHUI (Baggio *et al.*, 2003)] have been reported. In most of these chain structures, besides the formate group, aqua, urea and formamide groups are also coordinated to the central atoms. Consequently, structurally non-equivalent metal atoms can be identified in these structures, in contrast to the situation for the title compound.

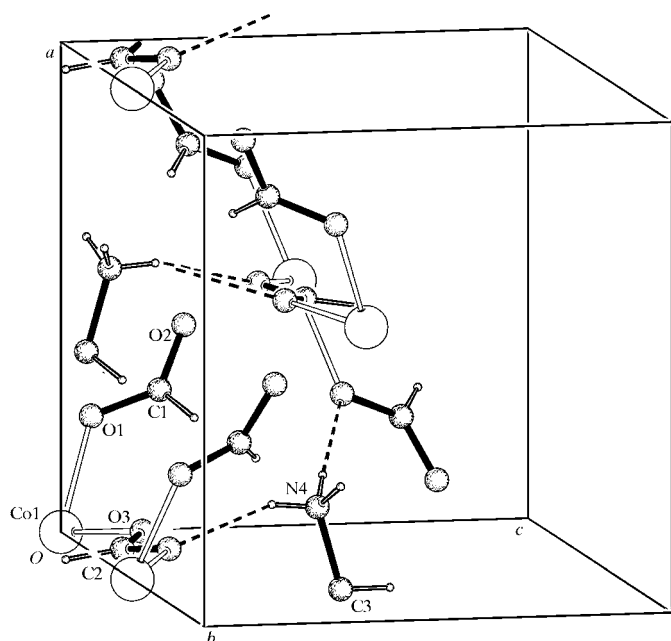


Figure 2
A packing diagram illustrating the hydrogen-bonding network.

A very similar structure to that of the title compound was reported for a complex with a central Cu^{II} ion (VINROZ; Nifontova *et al.*, 1990). The two structures are isostructural, with similar cell parameters and the same space group (the *b* and *c* vectors are transposed). In the copper analog, the Cu–O bonds on one axis of the octahedron are significantly longer (2.389 Å) than the remaining metal–oxygen bonds (1.955 and 2.011 Å). Thus, the copper complex exhibits a greater deviation from regular octahedral coordination, the octahedron being elongated, with *D_{4h}* symmetry. Both C–O–C angles are slightly larger in the copper complex than in the cobalt complex. The same system of hydrogen bonds was identified in the two complexes.

The formation of protonated methylamine is quite common and has been observed in many structures.

Experimental

A solution of CoCl₂·6H₂O (0.476 g, 2 mmol) in dry ethanol (5 ml) was added to a solution of the ligand *L* [0.356 g, 1 mmol, as a condensation product of 2-pyridinecarboxaldehyde *N*-oxide and triethylenetetramine (Boča, Valigura & Linert, 2000)] in dry ethanol (10 ml). The mixture was stirred for 2 h at room temperature. The resulting green solid was filtered off, washed with dry ethanol and dried for 3 h at 323 K. The resulting complex, [Co₂(*L*)Cl₄]·2H₂O, was recrystallized isothermally from methylformamide for two months until single crystals suitable for X-ray analysis were obtained. IR spectra were measured on single crystals. Asymmetric N–H deformation (*E*) vibrations at 1563 cm⁻¹ and symmetric N–H deformation (*A₁*) vibrations at 1486 cm⁻¹ were observed, as well as weak asymmetric N–H valence (*E*) vibrations at 3097 cm⁻¹ and symmetric N–H valence (*A₁*) vibrations at 3014 cm⁻¹. Lowering of the intensity of these vibrations can arise from the involvement of NH groups in the hydrogen-bonding network. Valence C–O vibrations (*A'*) at 1102 cm⁻¹ and deformation COO vibrations (*A'*) at 669 cm⁻¹ were observed. The lowering of the valence C–O frequency upon coordination (in comparison with pure formic acid) has been observed.

Crystal data

(CH₆N)[Co(CHO₂)₃]
M_r = 226.05
 Orthorhombic, *Pnma*
a = 8.4069 (9) Å
b = 11.7100 (10) Å
c = 8.1075 (9) Å
V = 798.14 (14) Å³
Z = 4
D_x = 1.881 Mg m⁻³

Mo Kα radiation
 Cell parameters from 899 reflections
 θ = 3.7–23.1°
 μ = 2.14 mm⁻¹
T = 300 (2) K
 Cube, brown
 0.24 × 0.24 × 0.24 mm

Data collection

Oxford Diffraction Xcalibur CCD diffractometer
 ω scans
 5931 measured reflections
 1173 independent reflections
 854 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.043
 θ_{max} = 30.1°
h = -11 → 9
k = -16 → 15
l = -11 → 11

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.049
wR(*F*²) = 0.160
S = 1.02
 1173 reflections
 76 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 0.39 e Å⁻³
 Δρ_{min} = -0.62 e Å⁻³

Table 1
Selected geometric parameters (Å, °) for (I).

C1—O2	1.245 (4)	O1—Co1	2.117 (2)
C1—O1	1.253 (4)	O2—Co1 ^{vi}	2.093 (2)
C2—O3	1.249 (4)	O3—Co1	2.107 (2)
C3—N4	1.414 (11)		
O2—C1—O1	125.0 (4)	O3—Co1—O3 ^{ix}	180
O3—C2—O3 ^v	123.5 (6)	O3—Co1—O1	92.07 (10)
O2 ^{vii} —Co1—O2 ^{viii}	180	O1—Co1—O1 ^{ix}	180

Symmetry codes: (v) $x, \frac{1}{2} - y, z$; (vi) $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$; (vii) $x - \frac{1}{2}, y, \frac{1}{2} - z$; (viii) $\frac{1}{2} - x, 1 - y, z - \frac{1}{2}$; (ix) $-x, 1 - y, -z$.

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

D—H...A	D—H	H...A	D...A	D—H...A
N4—H4A...O1 ^s	0.89 (4)	2.01 (4)	2.893 (4)	170 (5)
N4—H4B...O3 ^{iv}	0.89 (1)	2.28 (2)	3.051 (5)	145 (3)
N4—H4B...O3 ^{xi}	0.89 (1)	2.28 (2)	3.051 (5)	145 (3)

Symmetry codes: (iv) $\frac{1}{2} + x, y, \frac{1}{2} - z$; (xi) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$.

All C3—H distances for the methyl group were restrained with a DFIX 0.96 (1) command (Sheldrick, 1997), the mutual distances of all three H atoms of the methyl group were restrained with a DFIX 1.46 (1) command and the N4...H distances for all three methyl H atoms were restrained with a DFIX 1.87 (2) command. All N4—H distances of the aminium group were restrained with a DFIX 0.89 (1) command. The H atoms on the formyl groups were included in the refinement at geometrically calculated positions and refined using a riding model. For all H atoms, $U_{iso}(H)$ values were constrained to be $1.2U_{eq}$ of the parent C atom.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2001); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2001); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1205). Services for accessing these data are described at the back of the journal.

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