Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.120$
$S = 0.959$
4111 reflections
244 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0457P)^2 + 0.5031P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.34$ e Å^{-3}
$\Delta\rho_{\min} = -0.38$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Zn—O5	2.028 (3)	O7—N6	1.219 (4)
Zn—O2	2.056 (3)	N1—C5	1.335 (5)
Zn—N1	2.132 (3)	N1—C1	1.341 (5)
Zn—N2	2.146 (3)	N2—C6	1.282 (5)
Zn—S	2.3744 (13)	N2—N3	1.373 (4)
S—C8	1.702 (4)	N3—C8	1.365 (5)
O1—C10	1.408 (5)	N4—C8	1.333 (5)
O1—C11	1.418 (6)	N4—C12	1.464 (5)
O2—N5	1.246 (5)	N4—C9	1.465 (5)
O3—N5	1.231 (5)	C5—C6	1.496 (5)
O4—N5	1.221 (5)	C6—C7	1.474 (6)
O5—N6	1.295 (4)	C9—C10	1.497 (7)
O6—N6	1.227 (4)	C11—C12	1.490 (7)
O5—Zn—O2	94.00 (13)	C8—N4—C9	126.7 (3)
O5—Zn—N1	86.35 (12)	C12—N4—C9	110.3 (3)
O2—Zn—N1	97.04 (13)	O4—N5—O3	120.9 (4)
O5—Zn—N2	135.52 (12)	O4—N5—O2	118.3 (4)
O2—Zn—N2	127.10 (13)	O3—N5—O2	120.7 (4)
N1—Zn—N2	73.76 (12)	O7—N6—O6	123.8 (4)
O5—Zn—S	105.59 (9)	O7—N6—O5	119.1 (4)
O2—Zn—S	107.43 (10)	O6—N6—O5	117.1 (4)
N1—Zn—S	151.63 (10)	N1—C5—C6	115.2 (3)
N2—Zn—S	80.01 (9)	C7—C6—C5	119.9 (4)
C10—O1—C11	110.5 (3)	N3—C8—S	121.4 (3)
C5—N1—C1	117.9 (3)	O1—C10—C9	112.2 (4)
C6—N2—N3	120.4 (3)	O1—C11—C12	111.9 (4)
C8—N3—N2	118.1 (3)	N4—C12—C11	108.1 (4)
C8—N4—C12	122.4 (4)		

H atoms except those in methyl groups of (1) were refined isotropically. H atoms in methyl groups of (1) and the H atoms of (2) were located geometrically by *TEXSAN* (Molecular Structure Corporation, 1995) and were not refined.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN*; program(s) used to solve structures: *TEXSAN*, *DIRDIF* (Beurskens *et al.*, 1992), *DIRDIF*94 (Beurskens *et al.*, 1994) and *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1085). Services for accessing these data are described at the back of the journal.

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Tetrakis(methylamine-*N*)(oxalato-*O*^{1},*O*^{2})-cobalt(III) perchlorate and tetrakis-(ethylamine-*N*)(oxalato-*O*^{1},*O*^{2})cobalt(III) perchlorate monohydrate

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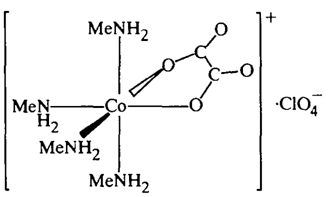
Abstract

In the title compounds, $[Co(C_2O_4)(CH_5N)_4]ClO_4$, (1), and $[Co(C_2O_4)(C_2H_7N)_4]ClO_4{\cdot}H_2O$, (2), the Co atom has a distorted octahedral coordination composed of four amine ligands and one oxalato ligand. The coordination

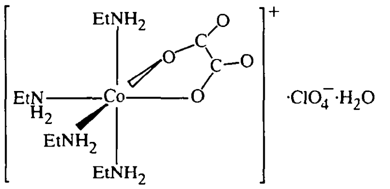
and oxalato bond distances in (1) and (2) are similar to the corresponding distances in $[Co(C_2O_4)(NH_3)_4]^+$. The Co—N—C angles are in the range 117.1 (4)–123.2 (2)°.

Comment

In our recent study on the unique acidity of the cobalt(III) complex with a hexafluoro-2,4-pentanedionato ligand (Kitamura *et al.*, 1990; Kitamura & Shibata, 1993), we prepared several cobalt(III) complexes bearing four monodentate ligands of methylamine, ethylamine or propylamine and one bidentate carbonate or hexafluoro-2,4-pentanedionate anionic ligand. Since a cobalt(III) complex with four primary amine ligands other than ammonia has not been reported, the title complexes, (1) and (2), were prepared and their structures analysed.



(1)



(2)

In (1) and (2), the Co atom has a distorted octahedral coordination composed of four amine ligands and one oxalato ligand. Complex (1) crystallizes in orthorhombic space group $Pca2_1$ and complex (2) crystallizes in monoclinic space group $P2_1/c$, both as racemates. For the perchlorate anion in (2), we have assumed two orientations on account of the crystal disorder. The coordination and oxalato bond distances in (1) and (2) are similar to the corresponding distances in $[Co(C_2O_4)(NH_3)_4]^+$, (3) (Bernal & Cetrullo, 1990; Bernal, Cetrullo & Myrczek, 1993; Bernal *et al.*, 1996). In (1) and (2), the acute bite angles O1—Co—O3 of the oxalato ligand are compensated by the obtuse O3—Co—N3 and O1—Co—N2 angles, respectively. The Co—N—C angles for the amines in (1) and (2) [range 117.1 (4)–123.2 (2)°] are similar to the Co—N—C angles [range 114–125°] for the tension-free 1,3-propanediamine chelates on cobalt(III) (Bernal, Myrczek *et al.*, 1993; Kitamura, Azuma, Minamoto *et al.*, 1997; Kitamura, Azuma & Ozawa, 1997). The N1—C3 distance in (1) and the N1—C3, N3—C7 and C9—C10 distances in (2) are short compared with the corresponding normal distances, *i.e.* N—C 1.48 and C—C 1.54 Å.

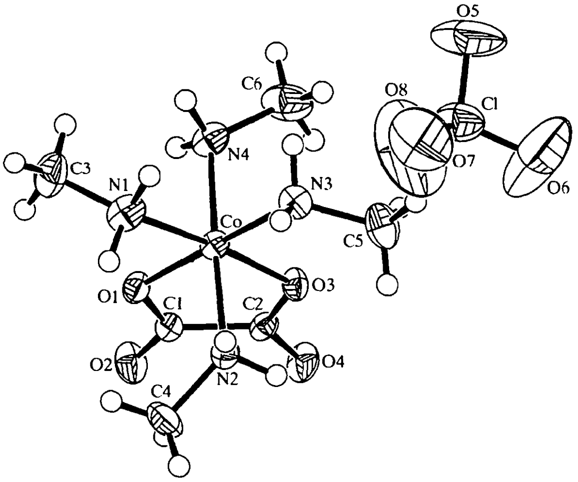


Fig. 1. A perspective view of (1). Displacement ellipsoids are drawn at the 50% probability level for non-H atoms. H atoms are included with displacement parameters of $B = 1.0$ Å^2.

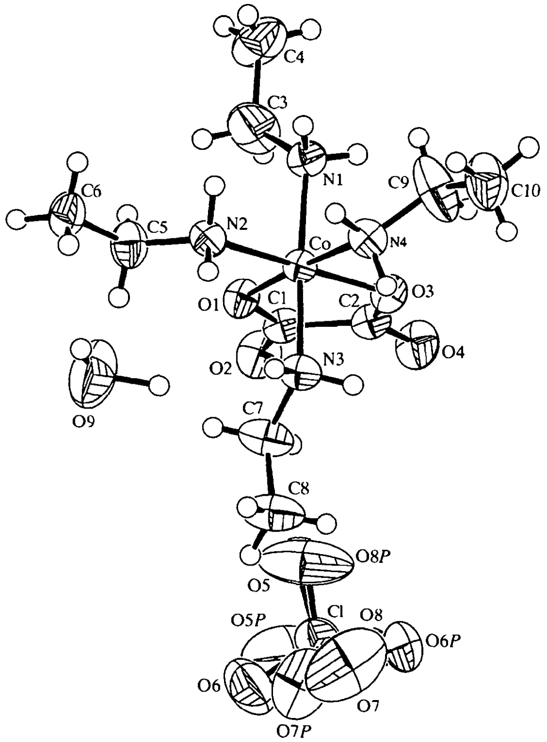


Fig. 2. A perspective view of (2). Displacement ellipsoids are drawn at the 50% probability level for non-H atoms. H atoms are included with displacement parameters of $B = 1.0$ Å^2.

Experimental

For the preparation of (1), an aqueous solution (6 ml) of $[Co(CO_3)(CH_3NH_2)_4]ClO_4\cdot H_2O$ (2 g) was mixed at 333 K with an aqueous solution (4 ml) of oxalic acid (0.5 g). After the gas evolution ceased, it was concentrated to 4 ml and cooled. A red solid substance [(1), yield 1 g], separated from the solution. For the preparation of (2), $[Co(CO_3)(CH_3CH_2NH_2)_4]ClO_4$ (5 g) was dissolved in the minimum amount of water. The solution was treated with oxalic acid dihydrate (1.6 g) and was concentrated at 343 K. A red solid substance [(2), yield 4 g], separated from the solution.

Compound (1)

Crystal data

$[Co(C_2O_4)(CH_5N)_4]ClO_4$
$M_r = 370.63$
Orthorhombic
$Pca2_1$
$a = 10.780\,(3)$ Å
$b = 11.004\,(3)$ Å
$c = 12.108\,(2)$ Å
$V = 1436\,(1)$ Å^3
$Z = 4$
$D_x = 1.714$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 12.1–12.8°$
$\mu = 1.418$ mm^{-1}
$T = 298.2$ K
Prismatic
0.33 × 0.30 × 0.05 mm
Red

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: ψ scans (North *et al.*, 1968)
$T_{min} = 0.748$, $T_{max} = 0.932$
2393 measured reflections
2393 independent reflections

2182 reflections with $I > 0$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 17$
3 standard reflections every 150 reflections intensity decay: 0.17%

Refinement

Refinement on F^2
$R(F) = 0.064$
$wR(F^2) = 0.048$
$S = 1.287$
2182 reflections
180 parameters
H-atom parameters not refined

$w = 1/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{max} = 0.0022$
$\Delta\rho_{max} = 0.62$ e Å^{-3}
$\Delta\rho_{min} = -0.59$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

Co—O1	1.912 (4)	O3—C2	1.282 (6)
Co—O3	1.877 (4)	O4—C2	1.230 (7)
Co—N1	2.015 (5)	N1—C3	1.435 (8)
Co—N2	1.990 (4)	N2—C4	1.483 (7)
Co—N3	1.973 (5)	N3—C5	1.480 (8)
Co—N4	1.983 (5)	N4—C6	1.481 (9)
O1—C1	1.287 (6)	C1—C2	1.555 (7)
O2—C1	1.220 (7)		
O1—Co—O3	86.1 (2)	Co—N2—C4	122.0 (3)
O3—Co—N3	95.5 (2)	Co—N3—C5	117.1 (4)
Co—N1—C3	120.6 (4)	Co—N4—C6	117.7 (4)

Table 2. *Hydrogen-bonding geometry (Å, °) for (1)*

D—H···A	D—H	H···A	D···A	D—H···A
N1^{i}—H1^{i}···O2	0.95	2.12	2.968 (7)	148
N3^{ii}—H12^{ii}···O4	0.95	2.05	2.962 (6)	160
N2^{ii}—H7^{ii}···O4	0.95	2.07	2.985 (6)	160

Symmetry codes: (i) $-x, -y, z - \frac{1}{2}$; (ii) $\frac{1}{2} - x, y, z - \frac{1}{2}$.

Compound (2)

Crystal data

$[Co(C_2O_4)(C_2H_7N)_4]$-$ClO_4{\cdot}H_2O$
$M_r = 444.75$
Monoclinic
$P2_1/c$
$a = 10.128$ (3) Å
$b = 13.538$ (3) Å
$c = 14.994$ (3) Å
$\beta = 103.23$ (1)°
$V = 2001.4$ (8) Å^3
$Z = 4$
$D_x = 1.476$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 14.8–15.0°$
$\mu = 1.034$ mm^{-1}
$T = 298.2$ K
Prismatic
0.40 × 0.30 × 0.25 mm
Red

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: ψ scans (North *et al.*, 1968)
$T_{min} = 0.746$, $T_{max} = 0.772$
5047 measured reflections
4790 independent reflections

4588 reflections with $I > 0$
$R_{int} = 0.017$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 17$
$l = -19 \rightarrow 18$
3 standard reflections every 150 reflections intensity decay: 5.10%

Refinement

Refinement on F^2
$R(F) = 0.066$
$wR(F^2) = 0.045$
$S = 1.259$
4588 reflections
272 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{max} = 0.0015$

$\Delta\rho_{max} = 0.56$ e Å^{-3}
$\Delta\rho_{min} = -0.51$ e Å^{-3}
Extinction correction: Zachariasen (1967) type 2 Gaussian isotropic
Extinction coefficient: 1.64×10^{-3}
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 3. *Selected geometric parameters (Å, °) for (2)*

Co—O1	1.917 (2)	N1—C3	1.454 (4)
Co—O3	1.912 (2)	N2—C5	1.478 (4)
Co—N1	1.980 (2)	N3—C7	1.447 (4)
Co—N2	1.959 (2)	N4—C9	1.461 (4)
Co—N3	1.987 (3)	C1—C2	1.543 (4)
Co—N4	1.979 (2)	C3—C4	1.497 (6)
O1—C1	1.278 (3)	C5—C6	1.512 (4)
O2—C1	1.225 (3)	C7—C8	1.518 (5)
O3—C2	1.282 (3)	C9—C10	1.484 (5)
O4—C2	1.224 (3)		
O1—Co—O3	85.34 (8)	Co—N2—C5	121.2 (2)
O1—Co—N2	93.42 (9)	Co—N3—C7	123.2 (2)
Co—N1—C3	123.1 (2)	Co—N4—C9	122.2 (2)

Table 4. *Hydrogen-bonding geometry (Å, °) for (2)*

D—H···A	D—H	H···A	D···A	D—H···A
O9—H29···O2	1.15 (8)	1.81 (9)	2.880 (4)	153 (7)
O9^{i}—H30^{i}···O3	1.05 (7)	2.49 (8)	2.963 (4)	107 (5)
N2^{ii}—H8^{ii}···O4	0.95	2.02	2.897 (3)	153
N2^{ii}—H9^{ii}···O8	0.95	2.16	3.093 (6)	169

$N1^{ii}—H1^{ii}\cdots O8$	0.95	2.17	3.073 (6)	158
$N3^{iii}—H16^{iii}\cdots O9$	0.95	2.12	3.049 (4)	165

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

The positions of the H atoms were idealized (C—H or N—H 0.95 Å), assigned isotropic displacement parameters B(H) = $1.2B_{eq}$(C or N), and allowed to ride on their parent C or N atoms. The H atoms in the water molecule were refined isotropically. An orientational disorder of the perchlorate anion was observed in compound (2).

For both compounds, data collection: *MSC/AFC Diffractometer Control* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1989); program(s) used to solve structures: *TEXSAN*; program(s) used to refine structures: *TEXSAN*; molecular graphics: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1068). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 1270–1272

Bis(1,3-dibutylimidazolidin-2-one-*O*)bis(nitrato-*O*,*O*′)dioxouranium(VI)

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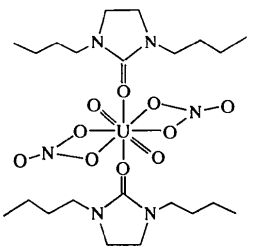
Abstract

In the title complex, $[UO_2(NO_3)_2(C_{11}H_{22}N_2O)_2]$, the central UO_2^{2+} cation is centrosymmetrically coordinated by six further O atoms, of which two are from the carbonyl groups of the 1,3-dibutylimidazolidin-2-one ligands and four from the two nitrate anions, forming a distorted hexagonal bipyramid. The average carbonyl U—O bond length is 2.345 (3) Å, which is the shortest value among similar dinitratodioxouranium complexes.

Comment

It has been reported that *N*,*N*-dialkylamides and *N*-alkylcaprolactam are effective agents for the extraction of actinides. We have found recently that 1,3-dibutylimidazolidin-2-one is even more effective for this purpose. Its stronger coordinating ability means that the carbonyl group conjugates with the two N atoms and the two alkyl groups supply electrons to the two N atoms. We have used 1,3-dibutylimidazolidin-2-one to extract UO_2 to give the title complex, (I), and this paper describes its X-ray crystallographic structure.



(I)

In (I), the UO_2^{2+} cation is centrosymmetrically coordinated by six further O atoms, two from the carbonyl groups of the 1,3-dibutylimidazolidin-2-one ligands and four from the two nitrate anions, thus forming a distorted hexagonal bipyramid similar to another UO_2^{2+} complex reported by Wang *et al.* (1995). Selected bond lengths and angles for (I) are given in Table 1 and the molecular