Properties and Reactivity of Metallocarboxylates. Crystal and Molecular Structure of the $-CO_2^{2-}$-Bridged "Polymer" $\{[Co^{III}(en)_2(CO_2)](ClO_4)\cdot H_2O\}_n$

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Introduction

Metallocarboxylates (η^1-CO_2 complexes) are important in several areas of catalysis, including that of CO_2 reduction.[2,3] In the early 1970s, Endicott, Hoffman, et al. described the preparation of metallocarboxylates via UV photolysis of oxalate complexes.[4] We extended the earlier studies of $Co(en)_2(H_2O)(CO_2H)^{2+}$ (en = ethylenediamine), synthesized the ester derivative *trans*-$Co(en)_2(CF_3CO_2)(C(O)OC_2H_5)^+$, and determined the crystal and molecular structure of the latter.[5] Despite many attempts under varying conditions, we were unable to crystallize the parent species $Co(en)_2(H_2O)(CO_2H)^{2+}$. Late in the course of that work we found that the pH dependence of spectra and the decomposition kinetics implied the existence of the kinetically very stable species $Co(en)_2(OH)(CO_2)$ at pH >5. We grew crystals from alkaline solutions of $Co(en)_2(OH)(CO_2)$, in the hopes of characterizing the structure of this unusual species. Instead, we obtained the $-CO_2^{2-}$-bridged polymeric species $\{[Co^{III}(en)_2(CO_2)](ClO_4)\cdot H_2O\}_n$, which is the subject of this note. Its structure and spectral properties are of interest as a point of comparison for the (few) other carboxylate-bridged species, and they are reported here.

Experimental Section

$\{[Co^{III}(en)_2(CO_2)](ClO_4)\cdot H_2O\}_n$. A solution of $Co(en)_2(OH)(CO_2)$ was prepared as described previously ("Method B").[5] The ca. 80 mL of $NaClO_4$-containing, phosphate-buffered solution was reduced in volume to ca. 10 mL on a rotary evaporator, with all transfers being carried out under argon. The concentrated solution (ca. 20 mM complex) was placed in a narrow tube and gently layered with diethyl ether. Crystals, which formed when the tube was left in the refrigerator (4 °C) overnight, were collected on a filter in an argon-filled glovebag. They were insoluble in acetonitrile, acetone, and dichloromethane but extremely soluble in water. The deuterated sample ($ND_2CH_2CH_2ND_2$ ligands instead of perprotio-en) was prepared in the same way except that the solution was evaporated to near dryness on the rotary evaporator and 8 mL of deaerated D_2O (Aldrich) was added under argon. The solution was stored in a freezer for several days, and the solid was collected from it, washed with ether, and used to prepare a Nujol mull on which the IR was run. From the undetectable residual intensities of the N–H stretch and deformation modes, D/H exchange was >90% complete. The chemical purities of the samples were established by comparison of their UV–vis spectra with those determined earlier.[5]

Warning: Perchlorate salts are potentially explosive and must be handled with care!

IR spectra were determined with a Mattson Polaris FT-IR spectrometer, ^{13}C NMR, on a Bruker AM-300 FT-NMR spectrometer, and UV–vis spectra on a HP 8452A instrument.

Collection and Reduction of X-ray Diffraction Data. The crystals of $\{[Co^{III}(en)_2(CO_2)](ClO_4)\cdot H_2O\}_n$ were orange prisms. They were very poor diffractors of X-rays. After studying many crystals, some of which were twinned and others of which did not diffract well, we chose a prism 0.20 × 0.15 × 0.18 mm for data collection. A temperature of 200 K and Cu Kα radiation were selected to maximize the quality of the diffraction data. The diffraction data indicated monoclinic symmetry, and the systematic absences $h0l$, $h + l = 2n + 1$, and $0k0$, $k = 2n + 1$, are consistent with the space group $P2_1/n$ (a nonstandard setting of $P2_1/c$, No. 14, C^5_{2h}).[6]

Crystal data and information about the data collection are given in Tables I and S1 (supplementary material).

Determination and Refinement of the Structure. The structure was solved[7] by standard Patterson heavy-atom methods. In the least-squares refinement,[7] anisotropic temperature parameters were used for all of the non-hydrogen atoms and the quantity $\sum w(|F_o| - |F_c|)^2$ was minimized. Hydrogen atoms on the ethylenediamine ligands were placed at calculated positions (X–H = 0.95 Å) and were allowed to "ride" on the C or N to which they were attached. A common isotropic thermal parameter was refined for all of these hydrogen atoms. Only one hydrogen atom on the water of crystallization could be located on a difference Fourier map,[7] and it was included in a fixed position with a fixed thermal parameter in the final refinement.

Final non-hydrogen atom positional parameters are listed in Table II, and selected interatomic distances and angles are given in Table III.

Results and Discussion

In light of the polymeric structure determined for the solid formed from concentrated aqueous solutions of $Co(en)_2(OH)(CO_2)$, we were concerned about the nature of the parent solutions. At pH 7 (0.03 M phosphate buffer, 0.06 M $NaClO_4$), the solutions followed Beer's law over the 0.2–2 mM concentration range. Thus there remains no evidence for oligomerization under the conditions of the original[5] kinetics and product studies.

The ^{13}C NMR spectrum of $Co(en)_2(CO_2)(ClO_4)$ (10 mM) dissolved in D_2O containing 0.1 M NaOD at 297 K (data collected for ≥15 h) contains a single signal below 250 ppm (reference CH_3OD at 49.0 ppm) at 49.6 ppm, which is assigned to the ethylenediamine carbons. (Since the ethylenediamines are trans to one another, all four ethylenediamine carbons are equivalent.) Thus the carbon in the CO_2 moiety could not be observed, probably because of both its long relaxation time and because of quadrupolar broadening by the cobalt, to which it is directly attached. The ethoxycarbonyl exhibits analogous behavior. NMR (0.01 M triflic acid/D_2O) for *trans*-$Co(en)_2(OD_2)(C(O)OC_2H_5)^{2+}$: $NH_2\mathit{C}H_2CH_2NH_2$, 44.2 ppm; $-CH_2\mathit{C}H_3$, 14.1 ppm; $O\mathit{C}H_2CH_3$, 65.6 ppm. NMR (0.01 M triflic acid/D_2O) for *trans*-$Co(en)_2(OD)(C(O)OC_2H_5)^+$: $ND_2\mathit{C}H_2\mathit{C}H_2ND_2$, 43.7 ppm; $-CH_2\mathit{C}H_3$, 14.2 ppm; $O\mathit{C}H_2CH_3$, 62.9 ppm. For the *cis*-bis(ethylenediamine) derivatives, the en region was more complicated and both formate and oxalate carbons could be found. *cis*-$Co(en)_2(HCO_2)_2^+$ in D_2O: en, 44.5, 44.6, 44.7 ppm (triplet); HCO_2^-, 175.4 ppm. *cis*-$Co(en)_2(C_2O_4)^+$ in 0.01 M triflic acid/D_2O: en, 43.6, 44.8 (weak), 45.7 ppm; $C_2O_4^{2-}$, 168.8 ppm.

Comparison of the IR spectra of protio and deuterio samples of $[Co(en)_2(CO_2)](ClO_4)\cdot H_2O$ suggests the following assignments: ν_{NH} 3322, 3277, 3158 cm^{-1}; δ_{NH} 1611 cm^{-1}; ν_{CO} 1645 (br), 1512 cm^{-1} (ν_{OH} 3583, 3518 cm^{-1}). For the N-deuterated species: ν_{ND} 2483, 2466, 2417 cm^{-1}; ν_{CO} 1640 (br), 1521 cm^{-1}. The ND deformation band was not resolved, probably because of its low intensity and masking by other bands. The shift of the 1512-cm^{-1} band to lower frequency in the deuterated

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[2] Behr, A. *Carbon Dioxide Activation by Metal Complexes*; VCH: New York, 1988; see also references therein.

[3] *Electrochemical and Electrocatalytic Reduction of Carbon Dioxide*; Sullivan, B. P., Ed.; Elsevier: Amsterdam, The Netherlands, 1992; see also references therein.

[4] Vaudo, A. F.; Kantrowitz, E. R.; Hoffman, M. Z.; Papaconstantinou, E.; Endicott, J. F. *J. Am. Chem. Soc.* **1972,** *94*, 6655.

[5] Katz, N. E.; Szalda, D. J.; Chou, M. H.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1989,** *111*, 6591–6601.

[6] *International Tables for X-ray Crystallography*, 3rd ed.; Kynoch Press: Birmingham, U.K., 1969; Vol I, p 99.

[7] Sheldrick, G. M. In *SHELX-76*; Schenk, H.; Olthof-Hazekamp, R., van Koningsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, The Netherlands, 1978; pp 34–42.

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Table I. Crystallographic Data for $\{[Co(H_2NCH_2CH_2NH_2)_2(CO_2)](ClO_4)\cdot H_2O\}_n$

formula	$[Co(C_2N_2H_8)_2(CO_2)](ClO_4)\cdot H_2O$
a, Å	9.295 (3)
b, Å	9.583 (5)
c, Å	14.334 (10)
β, deg	93.34 (4)
V, Å^3	1275 (2)
Z	4
fw	340.6
space group	$P2_1/n$
ρ(calcd), g cm^{-3}	1.774
λ(graphite monochromatized), Å	1.540 51 (Cu Kα)
μ, cm^{-1}	126
transm coeff	0.1141–0.3115
R^a	0.090
$R_w{}^a$	0.092
max shift/error, final cycle	≤0.01
T, K	200

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = \{\sum[w(|F_o| - |F_c|)^2]/\sum[w|F_o|^2]\}^{1/2}$.

Table II. Positional Parameters for the Non-Hydrogen Atoms in $\{[Co^{III}(en)_2(CO_2)](ClO_4)\cdot H_2O\}_n{}^a$

atom	x	y	z	U_{eq},[b] Å^2
Co	0.2395 (3)	–0.0167 (3)	0.22141 (18)	0.023
C(5)	0.274 (3)	0.2844 (19)	0.2948 (15)	0.061
O(1)	0.2995 (15)	0.2378 (11)	0.3729 (8)	0.048
O(2)	0.2501 (13)	0.2089 (11)	0.2215 (8)	0.036
N(1)	0.4228 (14)	–0.0307 (14)	0.2959 (9)	0.031
C(1)	0.5431 (19)	–0.0483 (19)	0.2374 (12)	0.041
C(2)	0.517 (2)	0.027 (2)	0.1464 (15)	0.063
N(2)	0.3579 (15)	–0.0021 (14)	0.1148 (9)	0.035
N(3)	0.0559 (15)	0.0078 (15)	0.1487 (10)	0.040
C(3)	–0.060 (2)	0.0360 (19)	0.2102 (12)	0.047
C(4)	–0.0356 (18)	–0.0525 (19)	0.2957 (12)	0.035
N(4)	0.1270 (16)	–0.0277 (14)	0.3258 (10)	0.046
Cl	0.2297 (6)	0.2875 (5)	–0.0563 (3)	0.041
O(11)	0.3818 (17)	0.2792 (17)	–0.0323 (13)	0.099
O(12)	0.168 (2)	0.4067 (16)	–0.0182 (10)	0.092
O(13)	0.1587 (15)	0.1675 (14)	–0.0233 (10)	0.060
O(14)	0.2123 (17)	0.2886 (14)	–0.1557 (9)	0.066
O(22)	0.1586 (19)	–0.2811 (17)	–0.0708 (10)	0.093

[a] Numbers in parentheses are errors in the last significant digit(s). [b] $U_{eq} = [U_{22} + (U_{11} + U_{33} + 2U_{13}(\cos\beta))/\sin^2\beta]/3$.

Table III. Bond Distances (Å) and Angles (deg) for $\{[Co^{III}(en)_2(CO_2)](ClO_4)\cdot H_2O\}_n$

	Cobalt–Ligand Distances		
Co–N(1)	1.962 (12)	Co–C(5)[a]	1.924 (20)
Co–N(2)	1.939 (14)	Co–O(2)	2.164 (11)
Co–N(3)	1.961 (14)		
Co–N(4)	1.878 (16)		
	Cobalt–Ligand Angles		
N(1)–Co–N(2)	85.3 (6)	N(2)–Co–O(2)	84.3 (5)
N(1)–Co–N(3)	177.0 (6)	N(3)–Co–N(4)	85.6 (6)
N(1)–Co–N(4)	93.9 (6)	N(3)–Co–C(5)[a]	90.3 (8)
N(1)–Co–C(5)[a]	92.7 (8)	N(3)–Co–O(2)	85.4 (5)
N(1)–Co–O(2)	91.7 (5)	N(4)–Co–C(5)[a]	90.3 (8)
N(2)–Co–N(3)	95.1 (6)	N(4)–Co–O(2)	94.8 (5)
N(2)–Co–N(4)	178.8 (6)	C(5)[a]–Co–O(2)	173.0 (8)
N(2)–Co–C(5)[a]	90.7 (8)		
	$-CO_2{}^{2-}$ Distances		
C(5)–O(1)	1.214 (19)	C(5)–O(2)	1.285 (18)
	$-CO_2{}^{2-}$ Angles		
O(1)–C(5)–O(2)	124 (2)	C(5)–O(2)–Co	125 (1)
O(1)[a]–C(5)[a]–Co	119 (1)	O(2)[a]–C(5)[a]–Co	117 (1)

[a] $0.5 - x, -0.5 + y, 0.5 - z$.

sample may be caused by the hydrogen-bonding interactions of both oxygens in the CO_2 group with the ethylenediamine amine hydrogens (see below). The position of the higher energy, C═O stretching band (1645 cm^{-1}) is the same as was observed for the ethoxycarbonyl,[5] but the origin of the 1512-cm^{-1} band is puzzling. It appears to be too high in frequency for the C—O stretch (expected value ≪1400 cm^{-1}).[8] Possibly the exterior of the solid (as opposed to crystal) dries (lacks the water of hydration) so that hydrogen bonding to the C═O differs from that in the interior of the material. The 1645-cm^{-1} band is very broad, consistent with a range of environments.

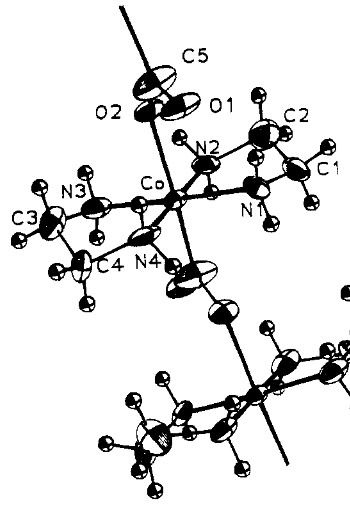

Figure 1. ORTEP view of two $Co(en)_2(CO_2)^+$ repeat units of the infinite polymeric chains found in the crystal lattice of $\{[Co^{III}(en)_2(CO_2)](ClO_4)\cdot H_2O\}_n$. The thermal ellipsoids are at the 50% probability level with hydrogen atoms represented with a thermal parameter $B = 1.0$ Å^2. The unlabeled repeat unit is related to the labeled atoms by the crystallographic 2-fold screw axis. The polymer is stabilized by six hydrogen bonds between the oxygens of the coordinated $CO_2{}^{2-}$ and the hydrogens of the ethylenediamine nitrogens.

Table IV. Comparison of the Structures of $Co-CO_2{}^{2-}$-Containing Species

	$Co(en)_2(CO_2)^+$	$Co(en)_2(CF_3CO_2)(CO_2Et)^{+\,a}$
d(Co–C), Å	1.924 (20)	1.922 (9)
d(Co–O), Å	2.164 (11)	2.046 (7)[b]
O_{coord}–C, Å	1.285 (18)	1.306 (10)[c]
O_{free}–C, Å	1.214 (19)	1.196 (9)
∠O–C–O, deg	124 (2)	123.7 (9)

[a] Katz, N. E.; Szalda, D. J.; Chou, M. H.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1989**, *111*, 6591–6601. [b] O═C(O)CF_3. [c] EtOC═O.

Description of the Structure. $\{[Co^{III}(en)_2(CO_2)](ClO_4)\cdot H_2O\}_n$ crystallizes as a "polymer" in which each cobalt is coordinated to the nitrogens of the trans, bidentate ethylenediamine ligands ($Co-N_{av}$ = 1.93 (4) Å), which form the equatorial plane of the octahedrally coordinated cobalt. One of the axial positions is occupied by the oxygen atom of the μ-$CO_2{}^{2-}$ group, and the other axial site is occupied by the carbon of the μ-$CO_2{}^{2-}$ group related by the crystallographic 2-fold screw axis. An ORTEP view of two repeat units of the polymeric chain and the numbering scheme used are shown in Figure 1. The polymeric structure is stabilized by a series of six proposed hydrogen bonds (see Table S5 (supplementary material)) between the amine hydrogens and the free and coordinated oxygen atoms of the $-CO_2{}^{2-}$ group. Hydrogen bonding interactions between the remaining amine hydrogens and the perchlorate anion and between the water of crystallization and the perchlorate anion serve to hold together the polymeric chain in the lattice. The large thermal ellipsoids for some atoms and the inequality of the Co–N bonds indicate some static disordering in the crystal lattice.

The structure of $\{[Co^{III}(en)_2(CO_2)](ClO_4)\cdot H_2O\}_n$ is most readily compared with that of *trans*-$Co(en)_2(CO_2Et)(O_2CCF_3)^+$.[5] (See Table IV.) The two $Co(en)_2$ structures differ in that one of the oxygen atoms of the CO_2 group is coordinated to another cobalt complex in the present case, while, in the ethoxycarbonyl,

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(8) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; John Wiley and Sons: New York, 1986.

it is bonded to an ethyl group. This difference does not significantly affect the bond parameters in the CO_2 portion of the molecule. The ethylenediamine bond distances and angles are similar, and in both cases, the cobalt lies 0.03 Å out of the plane of the four nitrogen atoms toward the axially coordinated carbon of the $-CO_2^{2-}$ or $-CO_2Et^-$ ligand. The Co–C distances are similar in the two compounds, 1.915 (21) Å (Co–CO_2) and 1.922 (9) Å (Co–CO_2Et), as are the bond parameters in the carboxylate portion of the molecule. The Co–O distance, 2.164 (11) Å, which is substantially greater here than that to the trifluoroacetate ligand (2.046 (7) Å) in *trans*-$Co(en)_2(CO_2Et)(O_2CCF_3)^+$ [5] and than those in *trans*-$Co(en)_2(C_2O_4)(H_2O)^+$, 1.891 (8) Å (Co–O_{ox}) and 1.931 (8) Å (Co–O_w),[9] confirms the strong trans effect of the C-bonded $-CO_2^{2-}$ ligand.

Although the present structure may be the first in which CO_2 bridging gives rise to a polymer, numerous examples of structures containing binuclear CO_2-bridged homo- or heterometallic species are known. Those containing Co–CO_2 moieties include LCoC(OH)OCoL^{3+} (L = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)[10] and L′CoC(O)OK (L′ = propyl-salen).[11] On the basis of the modest basicity of the carboxylate oxygen in $Co(en)_2(H_2O)(CO_2)^+$ (the pK_a of $Co(en)_2(H_2O)(CO_2H)^+$ is 2.5[5]), the coordination of this oxygen to cobalt in the solid-state polymer is not surprising, given that packing forces are operative. This Co–O bond is not, however, likely to persist in aqueous solution, given the relative abundance of superior ligands typically available in our solutions. Indeed, again the behavior of the present system finds precedent in that of the ethoxycarbonyl derivative. The latter can be obtained as crystals only in the presence of trifluoroacetate. However, the trifluoroacetate is very rapidly released when the crystals are dissolved in water or acetonitrile.[5]

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Supplementary Material Available: Tables of crystallographic data collection parameters, anisotropic thermal parameters for non-hydrogen atoms, calculated hydrogen atom positions, bond distances and angles, and proposed hydrogen bonding parameters (5 pages). Ordering information is given on any current masthead page.

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(9) Miskelly, G. M.; Clark, C. R.; Simpson, J.; Buckingham, D. A. *Inorg. Chem.* **1983**, *22*, 3237–3241.

(10) Fujita, E.; Szalda, D. J.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1988**, *110*, 4870–4871.

(11) Fachinetti, G.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc.* **1978**, *100*, 7405–7407.