N5	0.5974 (2)	0.0634 (1)	0.19421 (7)	3.28 (3)
C11	0.0636 (2)	0.2977 (1)	0.2376 (1)	3.70 (4)
C12	−0.0750 (2)	−0.1416 (1)	0.23520 (9)	2.83 (3)
C13	0.0310 (2)	0.1001 (1)	0.38010 (6)	2.01 (3)
C21	0.7362 (2)	−0.1260 (2)	0.04070 (9)	3.52 (4)
C22	0.6729 (2)	−0.1042 (2)	0.09261 (8)	3.25 (4)
C23	0.3915 (2)	−0.2019 (1)	−0.07106 (7)	2.26 (3)
C5	0.4812 (2)	0.0783 (1)	0.17651 (6)	2.16 (3)

Table 2. Selected geometric parameters (Å, °)

Co1—N11	1.947 (1)	Co2—N21	1.954 (1)
Co1—N12	1.945 (1)	Co2—N22	1.953 (1)
Co1—N13	1.896 (1)	Co2—N23	1.901 (1)
N11—Co1—N11^i	87.01 (5)	N21—Co2—N22	86.61 (6)
N11—Co1—N12	178.49 (5)	N21—Co2—N23	90.08 (6)
N11—Co1—N12^i	93.28 (5)	S13—C13—N13	178.6 (1)
N12—Co1—N12^i	86.48 (5)	S23—C23—N23	178.6 (1)
N13—Co1—N13^i	178.54 (6)	S5—C5—N5	176.7 (2)
N11—Co1—N11^i—C11^i	−12.7 (1)	N22—Co2—N21—C21	11.5 (1)
Co1—N11—C11—C11^i	35.6 (2)	Co2—N21—C21—C22	−37.0 (2)
N11—C11—C11^i—N11^i	−47.1 (2)	N21—C21—C22—N22	51.1 (2)
Co1—N12—C12—C12^i	39.3 (2)	C21—C22—N22—Co2	−40.6 (2)
N12—C12—C12^i—N12^i	−51.5 (2)	C22—N22—Co2—N21	16.6 (1)
N12—Co1—N12^i—C12^i	−14.3 (1)		

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

The space group was determined by systematic absences (*hkl* with *h* + *k* odd, *h0l* with *l* odd) and successful refinement of a centrosymmetric model.

Programs used include *SDP* (Frenz, 1978), *ORTEP* (Johnson, 1965) and *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978).

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Guanidinium β-cis-(Carbonato-O,O')-(N,N'-ethylenediaminediacetato-N,N',O,O'')-cobaltate(III)

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### Abstract

The title compound {aminomethanamidinium Λ-*uns-cis*-(*R,R*)-carbonato(*N,N'*-ethylenediaminediacetato)cobaltate(III), [C(NH$_2$)$_3$][Co(C$_6$H$_{10}$N$_2$O$_4$)(CO$_3$)]} crystallizes in the space group $P2_1/c$. The guanidinium cations and amino groups on the edda ligand form a complex network of eight to ten hydrogen bonds to both the coordinated and uncoordinated O atoms of the edda carboxylate groups and the carbonate ligands of neighbouring chelate anions. The hydrogen bonding between the guanidinium cations and carbonate ligands neither resembles that in guanidinium bicarbonate nor that between arginine and bound carbonate in ferrilactoferrin, an iron-binding protein which contains a carbonate ligand on the Fe^{3+} ion. Bond lengths and angles in the Co^{III} coordination sphere are not significantly different from those of other Co^{III} carbonate complexes or other Co^{III} edda complexes.

Comment

The structure determination of the title compound, (I), was carried out in order to compare the mode of interaction between the guanidinium cation and the carbonate ligand of the Co atom with that between guanidinium and the free bicarbonate anion (Baldwin, Denner, Egan & Markwell, 1986), as well as that

between the guanidinium group of arginine 121 and the carbonate ligand of Fe[III] in lactoferrin (Shongwe et al., 1992).

(I)
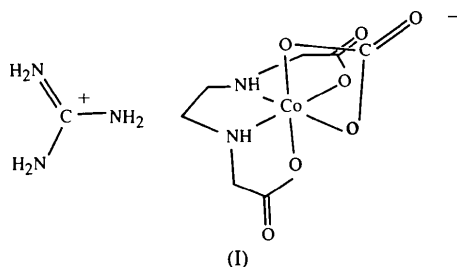
The structure of (I) is shown in Fig. 1. The bond lengths and angles in the coordination sphere of the Co[III] atom are not significantly different (Table 2) from those in other Co[III]–carbonato complexes (Palmer & van Eldik, 1983) or in other Co[III]–edda complexes, such as [Co(edda)(picolinato)] (Billing, Dobson, Pattrick & Carlton, 1991), [Co(edda)(R-1,2-diaminopropane)]Cl.-H₂O (Halloran, Caputo, Willett & Legg, 1975) and [Co(edda)(ethylenediamine)]ClO₄ (Chuklanova, Polynova, Sobolev & Porai-Koshits, 1984). The complex anion crystallizes as the Λ geometric isomer. The three chelate rings of edda have a δλλ conformation and an R,R nitrogen configuration, unlike [Co(edda)(picolinato)] and [Co(edda)(R-1,2-diaminopropane)]Cl.H₂O which each have a δλδ conformation and R,S nitrogen configuration.

The complete network of hydrogen bonds to one asymmetric unit in the unit cell is shown in the packing diagram (Fig. 2). All the hydrogen bonds are N—H···O bonds and the N···O lengths range from 2.81 to 3.19 Å, while the N—H···O angles lie between
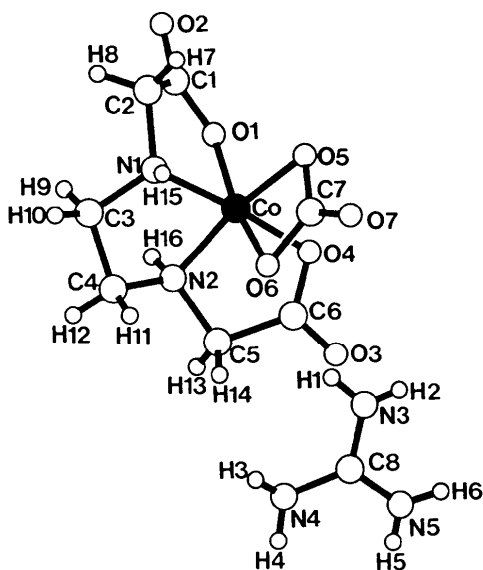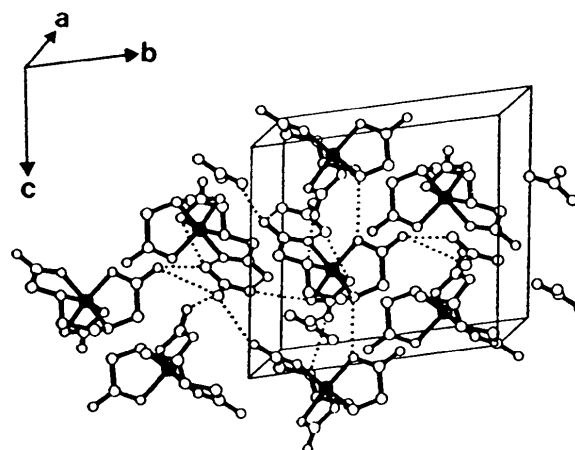

Fig. 2. Packing diagram of (I) showing all hydrogen bonds to one asymmetric unit. Guanidinium cations and chelate anions from neighbouring unit cells are included where they are hydrogen bonded to the asymmetric unit shown.

123.0 and 175.4°. These are all in the range typical for N—H···O bonds (Schuster, Zundel & Sandorfy, 1976; Pimentel & McLellan, 1960). There are two possible bifurcated hydrogen bonds from each guanidinium cation to neighbouring anions, N(4)—H(4)···O(7),O(2) and N(5)—H(6)···O(4),O(5). The hydrogen bonding between the guanidinium cations and the coordinated carbonate anions does not resemble that in guanidinium bicarbonate (Baldwin et al., 1986), where each guanidinium cation forms two hydrogen bonds to one neighbouring bicarbonate anion and one hydrogen bond to another. It also does not resemble the hydrogen-bonding interaction between arginine and coordinated carbonate in lactoferrin (Shongwe et al., 1992), where Arg 121 forms two hydrogen bonds to one of the coordinated O atoms of the carbonate.

The guanidinium cation does not appear to influence the structure of the coordination sphere of the Co[III] atom. This is in agreement with the observation that very high concentrations of guanidinium salts do not influence the rate of aquation of (I) to [Co(edda)(H₂O)(OH)] (Egan, 1988). Aquation is known to proceed by ring opening to a monodentate bicarbonate complex (Garnett & Watts, 1974b; van Eldik, Dasgupta & Harris, 1975; van Eldik, Spitzer & Kelm, 1983). In contrast, the guanidinium ion in solution is known to have a marked accelerating effect on the peroxidase activity of the Fe[III] porphyrin, microperoxidase-8, due to hydrogen bonding with the substrate HO₂⁻ (Baldwin, Marques & Pratt, 1985).

Fig. 1. Molecular structure of (I).

Experimental

Potassium [Co(edda)CO₃] was prepared according to published methods (Garnett & Watts, 1974a), but the α- and β-cis isomers were not separated since the former converts to the

latter in solution over a period of about 7 h at 293 K (van Eldik, Dasgupta & Harris, 1975). The solution was allowed to evaporate to dryness at 277 K and the potassium salt was recrystallized from ethanol/water. This was converted to the guanidinium salt by passage of an aqueous solution down a Dowex 50W–X8, 50–100 mesh strong-acid ion-exchange column in the guanidinium form. The needles were recrystallized from aqueous solution by slow vapour diffusion of ethanol. The density D_m was measured by flotation in a mixture of tetrachloromethane and dibromoethane.

Crystal data

[C(NH$_2$)$_3$][Co(C$_6$H$_{10}$-N$_2$O$_4$)(CO$_3$)]	Mo $K\alpha$ radiation
$M_r = 353.19$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 25
$P2_1/c$	reflections
$a = 11.631\,(3)$ Å	$\theta = 15.9–18.7°$
$b = 11.0660\,(10)$ Å	$\mu = 1.322$ mm^{-1}
$c = 10.563\,(2)$ Å	$T = 293\,(2)$ K
$\beta = 99.04\,(2)°$	Rectangular needle
$V = 1342.7\,(4)$ Å^3	$0.56 \times 0.06 \times 0.05$ mm
$Z = 4$	Purple
$D_x = 1.747$ Mg m^{-3}	
$D_m = 1.76$ Mg m^{-3}	

Data collection

Nonius CAD-4 diffractometer	3912 observed reflections
	$[I > 2\sigma(I)]$
$\omega/2\theta$ scans	$R_{\text{int}} = 0.0287$
Absorption correction:	$\theta_{\text{max}} = 29.97°$
ψ scans (North, Phillips & Mathews, 1968)	$h = 0 \rightarrow 16$
	$k = 0 \rightarrow 15$
$T_{\text{min}} = 0.874$, $T_{\text{max}} = 0.999$	$l = -14 \rightarrow 14$
4089 measured reflections	3 standard reflections
3912 independent reflections	frequency: 60 min
	intensity decay: random fluctuations

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + 0.1P^2]$
$R(F) = 0.0349$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.0810$	$(\Delta/\sigma)_{\text{max}} = -0.002$
$S = 0.906$	$\Delta\rho_{\text{max}} = 0.510$ e Å^{-3}
3912 reflections	$\Delta\rho_{\text{min}} = -0.396$ e Å^{-3}
210 parameters	Extinction correction: none
H-atom positions recalculated before each cycle of least-squares refinement	Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C)

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

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

	x	y	z	U_{eq}
Co	0.3006 (1)	0.2294 (1)	0.0991 (1)	0.023 (1)
O(1)	0.4107 (1)	0.2541 (2)	-0.0145 (1)	0.030 (1)
O(2)	0.5991 (2)	0.2895 (2)	-0.0116 (2)	0.043 (1)
O(3)	0.0147 (2)	0.1751 (2)	-0.1372 (2)	0.050 (1)
O(4)	0.1918 (1)	0.1521 (1)	-0.0291 (2)	0.031 (1)
O(5)	0.3572 (1)	0.0794 (1)	0.1740 (2)	0.029 (1)
O(6)	0.2117 (1)	0.1793 (2)	0.2254 (2)	0.030 (1)
O(7)	0.2606 (2)	0.0032 (2)	0.3257 (2)	0.043 (1)
N(1)	0.4050 (2)	0.3241 (2)	0.2176 (2)	0.029 (1)
N(2)	0.2177 (2)	0.3743 (2)	0.0462 (2)	0.029 (1)
N(3)	-0.0476 (2)	0.0964 (2)	0.1587 (3)	0.043 (1)
N(4)	-0.1532 (2)	0.2713 (2)	0.1433 (3)	0.049 (1)
N(5)	-0.2259 (2)	0.1048 (2)	0.0318 (3)	0.048 (1)
C(1)	0.5134 (2)	0.2826 (2)	0.0427 (2)	0.030 (1)
C(2)	0.5234 (2)	0.3055 (3)	0.1851 (2)	0.035 (1)
C(3)	0.3672 (2)	0.4530 (2)	0.2046 (3)	0.040 (1)
C(4)	0.2373 (2)	0.4558 (2)	0.1581 (2)	0.037 (1)
C(5)	0.0972 (2)	0.3382 (2)	-0.0033 (3)	0.037 (1)
C(6)	0.0987 (2)	0.2133 (2)	-0.0634 (2)	0.036 (1)
C(7)	0.2761 (2)	0.0807 (2)	0.2462 (2)	0.030 (1)
C(8)	-0.1434 (2)	0.1569 (2)	0.1113 (2)	0.034 (1)

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

Co—O(1)	1.907 (2)	Co—O(4)	1.905 (2)
Co—N(1)	1.914 (2)	Co—N(2)	1.909 (2)
Co—O(5)	1.910 (2)	Co—O(6)	1.895 (2)
O(1)—Co—N(1)	85.04 (7)	N(1)—Co—N(2)	88.32 (8)
N(2)—Co—O(4)	85.40 (8)	N(1)—Co—O(5)	93.62 (8)
O(5)—Co—O(6)	69.24 (7)	Co—O(6)—C(7)	89.99 (13)

The structure was solved by the Patterson method using *SHELXS*86 (Sheldrick, 1985) and refined using *SHELXL*93 (Sheldrick, 1993).

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Diiron Complex with Three Bridging Silyl Substituents

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Abstract

The crystal structure of hexacarbonyl-μ-(chloromethyl-silyl)-bis[μ-(dimethylsilyl)]diiron(*Fe—Fe*), [Fe$_2$(CH$_3$Cl-Si)(C$_2$H$_6$Si)$_2$(CO)$_6$], has been determined. The Fe—Fe distance is 2.705 (1) Å and the Fe—Si distances are 2.322 (3) Å. The combination of the sixfold screw axis and the uniqueness of the bridging SiMeCl moiety create rotational disorder within the unit cell.

Comment

The structure determination of the title compound, (I), was undertaken to establish its molecular structure. The title compound was synthesized *via* an apparent silylene-transfer reaction. Because of the low yield and low solubility, no spectroscopic evidence was available for any structural conclusions. However, crystals suitable for X-ray crystallography were available and the structure solution is given here.

(I)
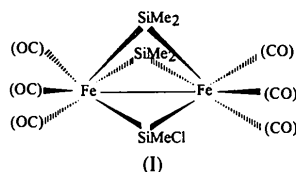
The structure of (I) is shown in Fig. 1, which illustrates the geometry of the structure as viewed down the Fe—Fe bond. Fig. 2 illustrates the packing of the title compound as viewed down a screw axis. The structure of (I) is similar to those of two other compounds which contain three Group 14 moieties bridging an Fe—Fe bond: Fe$_2$(CO)$_9$ (Cotton & Troup, 1974) and [Fe$_2$(μ-GeMe$_2$)$_3$(CO)$_3$] (Elder & Hall, 1969). Similarities are especially apparent with the latter compound. The Si and Ge compounds have similar unit-cell dimensions and both structures are solved in the centrosymmetric space group $P6_3/m$. The Fe—Fe bond distance in the silicon complex [2.705 (1) Å] is shorter than in the germanium complex [2.750 (11) Å]. Both Fe—Fe distances are significantly longer than that found in Fe$_2$(CO)$_9$ [2.523 (1) Å]. There is no lengthening of the Fe—Si bonds within the three-membered rings of (I) with respect to Fe—Si bonds in non-cyclic species. The Fe—Si distance of 2.322 (3) Å in (I) is well within the known range of Fe—Si single-bond distances (2.216–2.491 Å) (Lukevics, Pudova & Sturkovich, 1989; Sheldrick, 1989).
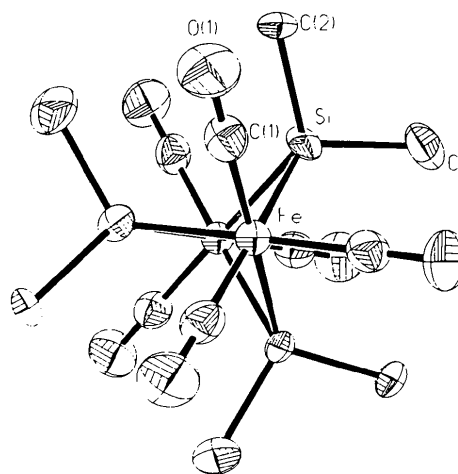
Fig. 1. Labeled ellipsoid diagram of (I). Displacement ellipsoids are drawn at the 50% probability level.
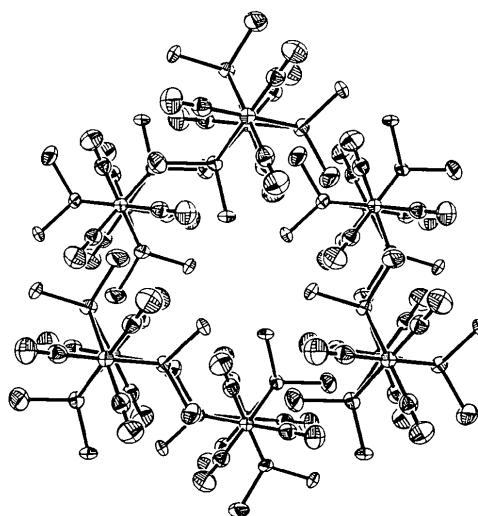
Fig. 2. Packing diagram of (I). Displacement ellipsoids are drawn at the 50% probability level.