

CARBONATOBIS(ETHYLENEDIAMINE)COBALI(III) CHLORIDE $[C_5H_{16}ClCoN_4O_3]$

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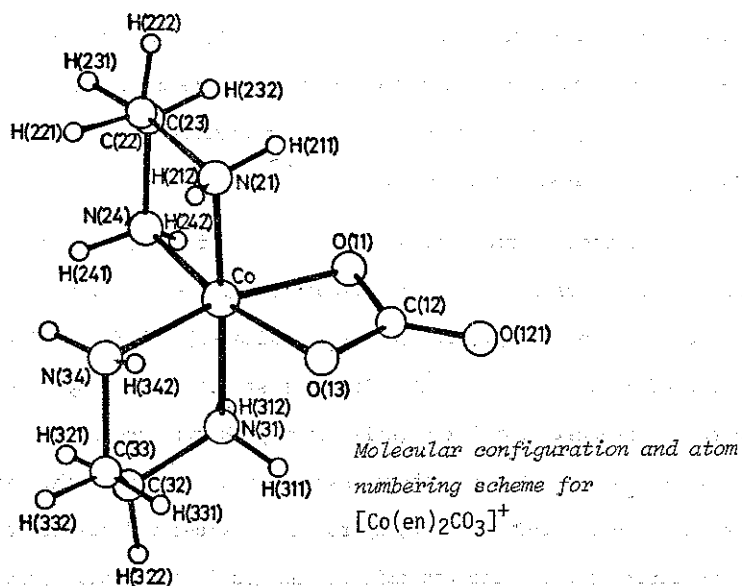
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Preliminary Information. The structure of the title compound was determined to provide further structural information on complexes of the type $[CoN_4CO_3]^+$, as part of a study on the effects of ionic, hydrogen and co-ordinate bonding on the structural parameters of chelated carbonate complexes. In this case N_4 is provided by two ethylenediamine ligands.

Crystal Data. $C_5H_{16}ClCoN_4O_3$, $M = 274.6$, Orthorhombic, space group $Pbc2_1$, ($Pca2_1$, C_{2v}^5 , No 29), $a = 11.077(3)$, $b = 10.751(3)$, $c = 8.550(3)\text{\AA}$, $U = 1018.2(5)\text{\AA}^3$, $D_m = 1.80(1)$, $D_c = 1.80\text{ g cm}^{-3}$ ($Z = 4$), $F(000) = 448$. Monochromatic Mo $K\alpha$ radiation ($\lambda = 0.71069\text{\AA}$), $\mu(\text{Mo } K\alpha) = 20.1\text{ cm}^{-1}$, $I = 295(1)\text{K}$.

Intensity Data and Refinement. The complex was prepared using the method of Springbørg and Schaffer (1974). Intensity data were collected from a single crystal ($0.10 \times 0.08 \times 0.16\text{ mm}$) using a Syntex PI four circle diffractometer. A unique set of data was collected in the range $2\theta < 55^\circ$, yielding 2137 independent reflections of which 1593 with $I > 2.5\sigma(I)$ were considered observed and used in the subsequent structure solution and refinement. Although intensity statistics indicated a non-centrosymmetric space group [$|E^2 - 1| = 0.76$], a trial structure was found using the direct methods approach of SHELX (Sheldrick, 1976) to give the $CoN_4(CO_3)Cl$ entity. A subsequent difference-Fourier synthesis gave the remaining non-hydrogens and full-matrix least-squares refinement in the space group $Pbc2_1$ reduced R to 0.059 with anisotropic temperature factors. A difference-Fourier synthesis indicated the positions of the hydrogen atoms; these were included and given the thermal parameter of their attached neighbour. The final value of R was 0.057, the weighed R' was 0.058, where $R' = [Ew||F_o| - |F_c||^2 / Ew|F_o|^2]^{1/2}$, and $w = 1.0 / (\sigma^2(F_o) + 0.000976 F_o^2)$.

Comments. The $[Co(en)_2CO_3]^+$ cation has Co(III) at its centre and is complexed to an asymmetric bidentate chelated carbonate group [Co-O(11), 1.895(7); Co-O(13), 1.934(7) \AA] and two ethylenediamines which complete the 'octahedral' first co-ordination sphere. There is



Atomic coordinates ($\times 10^4$) with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Co	2109 (1)	5696 (1)	2500
Cl	4580 (2)	2614 (2)	2444 (7)
O(11)	1884 (6)	7354 (7)	1808 (9)
C(12)	915 (7)	7478 (8)	2735 (9)
O(121)	343 (7)	8444 (8)	2899 (10)
O(13)	699 (6)	6429 (7)	3466 (10)
N(21)	1168 (7)	5024 (8)	811 (10)
C(22)	1987 (12)	4336 (13)	-205 (19)
C(23)	3119 (10)	5031 (13)	-321 (15)
N(24)	3544 (7)	5297 (8)	1290 (11)
N(31)	3087 (6)	6303 (7)	4290 (4)
C(32)	3464 (11)	5232 (13)	5311 (17)
C(33)	2376 (12)	4353 (13)	5351 (17)
N(34)	2092 (8)	4104 (7)	3654 (10)

a pseudo two-fold symmetry axis along the O(121)-C(12)-Co direction. The structural constraints imposed on the molecule by the two ethylenediamine groups prevent the compound crystallizing in the centrosymmetric space group *Pbcm*.

The carbonate group is similar to those found in other carbonato complexes of cobalt(III) (Table 1) with significant distortion from the free ion D_{3h} symmetry [C-O (co-ordinated) = 1.31, 1.34 Å and C-O (unco-ordinated) = 1.22 Å]. Previous structural and spectroscopic studies on carbonate complexes (Krishnamurty, Harris and Sastri, 1970 and references therein) have shown that the π electrons of the carbonate group can be polarized by ionic, hydrogen, covalent and co-ordinate bonding interactions, with concomitant changes in structural parameters. However, in these complexes, the considerable variation of hydrogen bond and cationic interactions with the carbonate group appears to have a minimal effect on the structural parameters. These results support the hypothesis that the effects observed are caused primarily by the central cobalt(III) cation. Certainly such a hypothesis can be used for these complexes to rationalize infrared spectroscopic observations in predicting bidentate chelation (Fujita, Martell and Nakamoto, 1962).

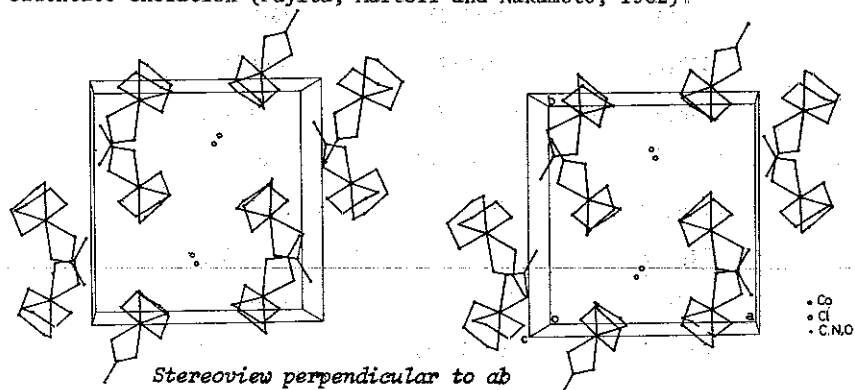


TABLE 1: COMPARATIVE Co-N, Co-O and C-O DISTANCES (Å) FOR A SERIES OF $[\text{Co}_n\text{CO}_3]^+$ COMPLEXES

Compound	Co-N(24)	Co-N(34)	Co-N(21)	Co-N(32)	Co-O(11)	Co-O(13)	C(12)-O(11)	C(12)-O(13)	C(12)-O(12)	Ref
$[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{Br}$	2.03(2)	2.03(2)	1.95(2)	1.93(2)	1.90(1)	1.90(1)	1.34(2)	1.34(2)	1.24(2)	a
$[\text{Co}(\text{en})_2\text{CO}_3]\text{Cl}$	1.944(8)	1.976(7)	1.922(8)	1.965(8)	1.895(7)	1.934(7)	1.34(1)	1.31(1)	1.22(1)	b
$[\text{Co}(\text{en})_2\text{CO}_3]\cdot 2\text{H}_2\text{O}$	1.943(3)	1.943(3)	1.940(3)	1.940(3)	1.907(2)	1.907(2)	1.306(3)	1.306(3)	1.234(6)	c
$[\text{Co}(\text{tn})_2\text{CO}_3]\text{ClO}_4$	1.94(2)	1.97(2)	1.95(2)	1.97(2)	1.89(1)	1.94(1)	1.32(2)	1.32(2)	1.22(2)	d
$[\text{Co}(\text{py})_4\text{CO}_3]\text{ClO}_4$	1.996(5)	2.004(4)	1.974(6)	1.985(7)	1.895(3)	1.892(3)	1.330(6)	1.319(5)	1.210(5)	e
$[\text{Co}(\text{phen})_2\text{CO}_3]\text{Br}\cdot 4\text{H}_2\text{O}$	1.949(6)	1.963(6)	1.940(6)	1.940(6)	1.889(4)	1.895(4)	1.332(2)	1.315(8)	1.213(8)	f
$[\text{Co}(\text{phen})_2\text{CO}_3]\text{Cl}\cdot 3\text{H}_2\text{O}$	1.93(1)	1.93(1)	1.94(1)	1.93(1)	1.88(1)	1.88(1)	1.33(2)	1.28(2)	1.20(2)	g
$[\text{Co}(3,8\text{-dimetrien})\text{CO}_3]\text{ClO}_4$	1.946(5)	1.935(5)	1.957(5)	1.956(5)	1.929(4)	1.901(4)	1.314(8)	1.296(8)	1.236(8)	h
$[\text{Co}(\text{C}_8\text{H}_{20}\text{N}_4)\text{CO}_3]\text{ClO}_4\cdot \text{H}_2\text{O}$	1.93(1)	1.93(1)	1.92(1)	2.02(2)	1.92(1)	1.91(1)	1.32(2)	1.31(2)	1.22(2)	i

a. Barclay and Hoskins, 1962. b. this work c. Bigoli, Ianfranchi, Leporati, Pellinghelli, 1980.

d. Geue and Snow, 1971. e. Kaas and Sørensen, 1973. f. Hennig, Sieler, Benedix, Kaiser, Sjölin and Lindqvist, 1980.

g. Guild, Hayden and Brennan, 1980. h. Toriumi and Saito, 1975. i. Loehlin and Fleischer, 1976.

Interatomic distances (Å) and angles (degrees) with estimated standard deviations in parentheses.

Co-O(11)	1.895(7)	C(12)-O(11)	1.34(1)
Co-O(13)	1.934(7)	C(12)-O(121)	1.22(1)
Co-N(21)	1.922(8)	C(12)-O(13)	1.31(1)
Co-N(24)	1.944(8)	C(23)-N(24)	1.48(1)
Co-N(31)	1.985(8)	N(31)-C(32)	1.50(1)
Co-N(34)	1.976(7)	C(32)-C(33)	1.53(2)
N(21)-C(22)	1.46(1)	C(33)-N(34)	1.51(1)
C(22)-C(23)	1.46(2)		
O(11)-Co-O(13)	69.1(4)	O(11)-Co-N(21)	92.7(4)
O(11)-Co-N(24)	98.6(4)	O(11)-Co-N(31)	90.2(4)
O(11)-Co-N(34)	165.9(4)	O(13)-Co-N(21)	92.1(4)
O(13)-Co-N(24)	167.7(4)	O(13)-Co-N(31)	88.7(4)
O(13)-Co-N(34)	97.6(4)	N(21)-Co-N(24)	87.7(4)
N(21)-Co-N(31)	177.1(4)	N(21)-Co-N(34)	92.5(4)
N(24)-Co-N(31)	92.1(4)	N(24)-Co-N(34)	94.7(4)
N(31)-Co-N(34)	84.5(4)	O(11)-C(12)-O(121)	124(1)
O(11)-C(12)-O(13)	110(1)	O(121)-C(12)-O(13)	125(1)
Co-N(31)-C(32)	110(1)	N(31)-C(32)-C(33)	105(1)
C(32)-C(33)-N(34)	105(1)	C(33)-N(34)-Co	109(1)
Co-N(21)-C(22)	108(1)	N(21)-C(22)-C(23)	108(1)
C(22)-C(23)-N(24)	108(1)	Co-O(13)-C(12)	90(1)
C(23)-N(24)-Co	106(1)	Co-O(11)-C(12)	91(1)

Acknowledgements. One of us (A.H. White) thanks the Australian Research Grants Committee for grants in support of this work. G.S. also thanks the Queensland Institute of Technology for leave to work on this project.

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Received: 23 February 1981