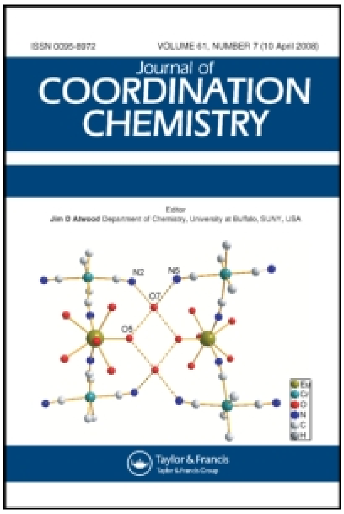

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THE PHENOMENON OF CONGLOMERATE CRYSTALLIZATION. XXII. SYNTHESIS AND STRUCTURAL CHARACTERISTICS OF μ-CARBONATO(*O*,*O′*)-*trans*-[Co(2,3,2-tet)(NO$_2$)]$_2$Cl$_2$.3H$_2$O[*]

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The unique, dinuclear, symmetrically μ-CO$_3$ bridged compound, μ-carbonato(*O*,*O′*)-*trans*-[Co(2,3,2-tet)(NO$_2$)]$_2$Cl$_2$.3H$_2$O (I), was prepared by hydrogen peroxide oxidation of Co^{+2} in the presence of the 2,3,2-tet polyamine ligand, followed by addition of NaNO$_2$. (I) crystallizes in the racemic space group $P2_1/n$ with cell constants $a = 9.187(1)$ Å, $b = 23.520(2)$, $c = 14.201(1)$, $\beta = 103.87(9)$, $V = 2978.90$ Å^3 and $d(Z = 4\,\text{mol/cell}) = 1.599\,\text{g cm}^{-3}$. Data were collected in the range $4° \leq 2\theta \leq 50°$, for a total of 5361 reflections, of which 3285 were independent and had $I \geq 3\sigma(I)$. These were used in the solution and refinement of the structure. The $F(hkl)_{obs}$ were corrected for absorption ($\mu = 13.540\,\text{cm}^{-1}$) using Psi scan curves of eight suitable reflections, leading to transmission coefficient adjustments ranging from 0.9049 to 0.9967. The structure was solved by Patterson methods. Convergence of the refinement using anisotropic thermal parameters for the heavy atoms and idealized hydrogens (fixed $B = 5.00$ Å^2) gave $R(F) = 0.0510$ and $R_w(F) = 0.0686$.

The molecule consists of two [*trans*-Co(2,3,2-tet)(NO$_2$)] fragments which are nearly perfect mirror images of each other. These are linked by a symmetric [(μ-CO$_3$)] bridge having two independent Co-C bonds of Co1–O5 = 1.917(2) and Co2–O6 = 1.911(2) Å. The third oxygen of the CO$_3$- bridge forms two short hydrogen bonds (1.919 and 1.988 Å) with a terminal –NH$_2$ hydrogen from each of the two adjacent polyamine ligands. The C–O distances of the bridging oxygens are, respectively, 1.291(3) and 1.229(3) Å in length. That of the unique C–O is 1.277(3), which fits the expectations of multiple bonding for this oxygen; yet, its length also reflects the multiple hydrogen bonding of this oxygen. The significance of this coordination mode (bridge bonding to metal and to adjacent ligands through hydrogen bonding) of the carbonato ligand may be established by its being an interesting model compound for biological species in which the metal is surrounded by –NH or –OH containing ligands to which the non-coordinating carbonato oxygen can be anchored.

Keywords: Cobalt(III), carbonato, 2,3,2-tet, dimer, X-ray structure

INTRODUCTION

Hereafter, we will use the abbreviations 2,3,2-tet and 3,2,3-tet to signify the tetradentate ligands $H_2N{-}CH_2{-}CH_2{-}NH{-}CH_2{-}CH_2{-}CH_2{-}NH{-}CH_2{-}CH_2{-}NH_2$ and $H_2N{-}CH_2{-}CH_2{-}CH_2{-}NH{-}CH_2{-}CH_2{-}NH{-}CH_2{-}CH_2{-}CH_2{-}NH_2$, respectively.

The number of well-characterized coordination compounds containing carbonato ligands is surprisingly low considering the ubiquity of the carbonato ion in nature, in general, and of the biological importance of the carbon cycle. Lactoferrin is an example of a metalloprotein whose structure[1] has been determined and shown to contain two Fe^{3+} centres which bind two carbonato (or bicarbonato) anions.

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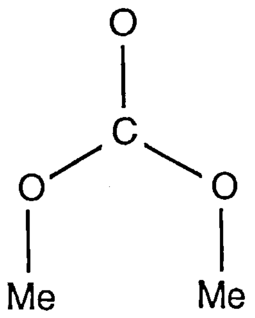
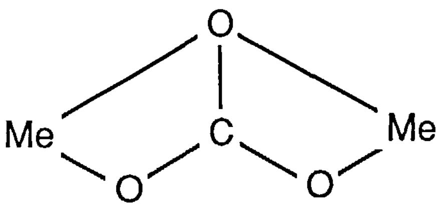
[*] On the occasion of Arthur Martell's 75th birthday.

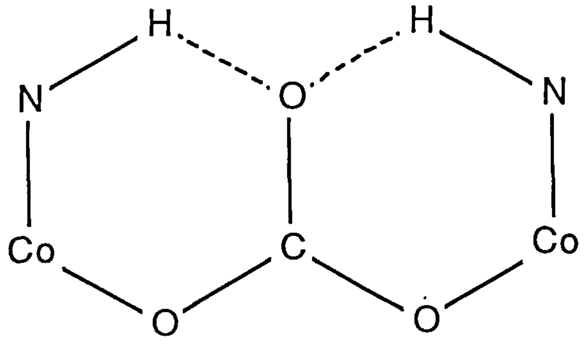
A thorough review of carbonato ligands and their stereochemistry was published by Einstein and Willis,[2] who devised a clever nomenclature to classify these ligands. Of the various modes they classify as known, those described as 2L,2M and 3L,2M come closest to the species we have observed and herein describe; however, what we have observed is, in fact, a geometrical isomer that shares characteristics of both the 2L,2M and 3L,2M species described by these authors and exemplified, in the case of 2L,2M, by compounds such as $KAgCO_3$[3], $Cs_4[Rh(CO_3)_4(H_2O)_2]\cdot 6H_2O$[4] and by $[(NH_3)_3Co(\mu\text{-}OH)_2(\mu\text{-}CO_3)Co(NH_3)_3]SO_4\cdot 5H_2O$;[5] and in the case of 3L,2M by $[(CuL)_2CO_3](ClO_4)_2$ (L = 2,4,4,9-tetramethyl-1,5,9-triazacyclododec-1-ene)[6] and by $[\{CuCl(\text{tetramethyl-1,3-propanediamine})\}_2]CO_3]$.[7]



2L, 2M Model



3L,2M Model



2L,2M + 2H Model

Thus, we have observed a new species which we now label as (2L,2M+ 1L,2H) which reflects the fact that two oxygens of the carbonato ligand bridge to two metals, while the third oxygen is a bridge to two amine hydrogens on adjacent metal ligands.

The compound described by Churchill[5] and ours are, thus far, the only examples known of carbonato-bridged dinuclear Co^{3+} compounds which are well characterized. Churchill *et al.*[5] reviewed all other claims to the preparation and isolation of others; whether, in fact, they were correctly formulated seems to be doubtful, for reasons described by them.[5]

Given the longstanding interest and masterful command of cobalt coordination chemistry Arthur Martell has amply demonstrated, and given his interest in the binding of small molecules by cobalt coordination compounds, it is with pleasure that we dedicate this addition to his chosen field of endeavours.

EXPERIMENTAL

*Synthesis of μ-carbonato(*O,O′*)-*trans*-[Co(2,3,2-tet)(NO$_2$)]$_2$Cl$_2$.3H$_2$O*

Dissolve 4.9 g (0.02 mol) $CoCl_2.6H_2O$ in 15 ml deionized water. Add 5 cm^3 30% hydrogen peroxide with stirring. Add 3.4 cm^3 *N,N′*-bis(2-aminoethyl)-1,3-propanediamine (0.02 mol) (Kodak) and begin heating. Add 1.4 g sodium nitrite (0.02 mol) and continue heating and stirring for 15 minutes at approximately 60°C. Approximately one gram of sodium chloride is dissolved in the mixture to encourage precipitation of the chloride salt. The mixture is filtered warm and then set aside to crystallize. The first crop of crystals did not yield a specimen suitable for an X-ray diffraction study. After recrystallization from deionized water at room temperature (21°C), a specimen suitable for a single crystal study was obtained.

Analyses

Performed by Galbraith Laboratories, Inc.[8] Theory %: C = 25.19, N = 19.58, H = 6.48, O = 22.37%; observed %: C = 24.47, N = 19.52, H = 6.63, O = 22.29.

X-ray diffraction

Data were collected with an Enraf-Nonius CAD-4 diffractometer operating with a Molecular Structure Corporation TEXRAY-230 modification[9] of the SDP-Plus software package.[10] The crystal was centred with data in the $18° \leq 2\theta \leq 25°$ range and examination of the cell constants and Niggli matrix[11] clearly showed it to crystallize in a primitive, monoclinic lattice whose systematic absences belong to those of the space group $P2_1/n$. The $F(hkl)_{obs}$ set was corrected for absorption using empirical curves derived from Psi scans[9,10] of eight reflections. The scattering curves were taken from Cromer and Waber's compilation.[12]

The structure was solved from the vectors of the Patterson function, which produced the two Co atoms. After refinement of the scale factor and their positional and isotropic thermal parameters, a difference Fourier map produced the atoms of the anion and many of the atoms of the cation. The missing atoms were found in subsequent difference maps. The three waters of hydration were also found there. Hydrogen atoms were added to the cation at idealized positions (C–H and N–H = 0.95 Å).

Refinement proceeded smoothly. Heavy atoms were assigned anisotropic thermal parameters, while the cation hydrogens were added at idealized, fixed positions after each cycle of refinement. The hydrogens of two waters were found at sensible positions and added to the atoms list, but not refined. Those of the third water were not found at satisfactory positions; however, their presence is clear from the agreement in %H and %O. The final $R(F)$ and $R_w(F)$ factors were 0.0510 and 0.0686, respectively. Details of data collection and processing are summarized in Table I.

TABLE I
Summary of data collection and processing parameters for µ-carbonato (*O,O*)-*trans*-[Co(2,3,2-tet)(NO$_2$)]$_2$ Cl$_2$.3H$_2$O.

Space group	$P2_1/n$
Cell constants	$a = 9.187(1)$ Å
	$b = 23.520(2)$
	$c = 14.201(2)$
	$\beta = 103.87(9)$
Cell volume	$V = 2978.90$ Å
Molecular formula	$Co_2Cl_2O_{10}N_{10}C_{15}H_{46}$
Molecular weight	715.36 gm mol^{-1}
Density (calc; Z = *4* mol/cell)	1.599 gm cm^{-3}
Radiation employed	MoKα (λ = 0.71073 Å)
Absorption coefficient	$\mu = 13.529$ cm^{-1}
Relative transmission coefficients	0.9049 to 0.9967
Data collection range	$4° \leq 2\theta \leq 50°$
Scan width	$\Delta\theta = 1.00 + 0.35\tan\theta$
Total data collected	5361
Data used in refinement*	3285
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.0510
$R_w = [\sum w^2(\|F_o\| - \|F_c\|)2/\sum\|F_o\|^2]^{1/2}$	0.0686
Weights used	$w = [\sigma(F_o)]^{-2}$

* The difference between this number and the total is due to subtraction of 2076 data which either were systematically absent (but collected for verification of space group), standards, or did not meet the criterion that $I \geq 3\sigma(I)$

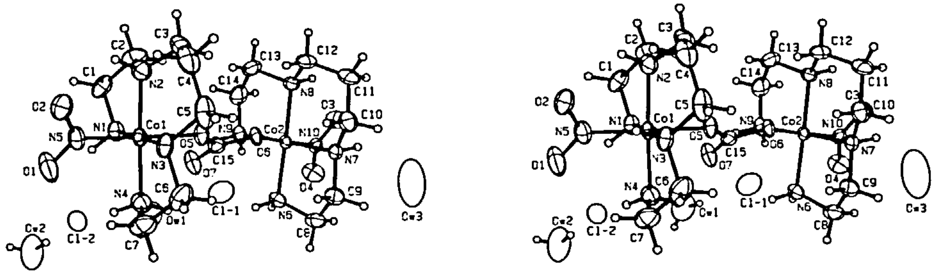


FIGURE 1 Stereoview of the molecule showing the labels used in the crystallographic study. Note the carbonato bridge and its orientation relative to the terminal –NH$_2$ hydrogens on the adjacent 2,3,2-tet ligand.

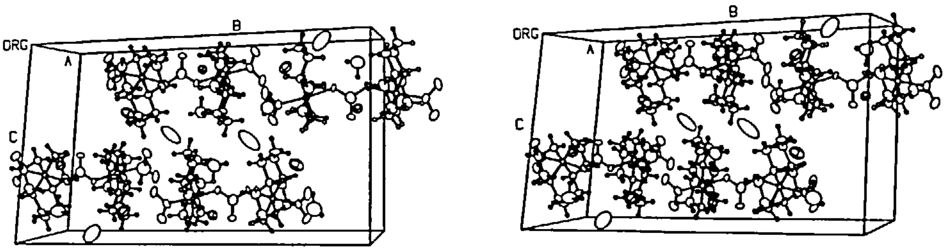


FIGURE 2 A packing diagram of the molecules in the monoclinic unit cell.

Figure 1 gives a labelled stereoview of the asymmetric unit; Figure 2 depicts in stereo the packing of the ions in the unit cell. Final positional and equivalent isotropic thermal parameters are given in Table II. Bond lengths and angles are listed in Table III, and torsion angles are given in Table IV.

TABLE II
Positional parameters and estimated standard deviations for μ-carbonato(*O*,*O'*)-[*trans*-Co(2,3,2-tet)(NO_2)]$_2$$Cl_2$.3$H_2O$.

Atom	*x/a*	*y/b*	*z/c*	*B*(Å^2)
Co1	0.2097(1)	0.06057(4)	0.31425(6)	1.59(2)
Co2	0.1995(1)	−0.18671(4)	0.31901(6)	1.48(2)
Cl1	0.2345(3)	−0.2126(1)	0.6423(2)	5.63(7)
Cl2	0.3630(2)	0.06266(9)	0.6270(1)	3.24(4)
Ow1	−0.2325(9)	0.1609(4)	0.1479(5)	7.3(2)
Ow2	0.619(1)	−0.0631(3)	0.1375(5)	7.7(2)
Ow3	0.5486(9)	−0.1667(4)	0.0197(6)	11.2(3)
O1	0.2659(8)	0.1595(2)	0.4221(4)	4.5(2)
O2	0.1348(6)	0.1726(2)	0.2788(4)	3.4(1)
O3	0.1002(7)	−0.2967(2)	0.2936(4)	4.2(2)
O4	0.2671(7)	−0.2854(2)	0.4237(4)	3.9(1)
O5	0.2146(6)	−0.0174(2)	0.2760(3)	2.2(1)
O6	0.2104(5)	−0.1098(2)	0.2777(3)	1.9(1)
O7	0.2361(6)	−0.0618(2)	0.4186(3)	3.0(1)
N1	0.1140(7)	0.0445(3)	0.4188(4)	2.3(1)
N2	0.0051(7)	0.0632(3)	0.2296(4)	2.5(1)
N3	0.3101(7)	0.0791(2)	0.2109(4)	2.2(1)
N4	0.4109(7)	0.0535(3)	0.3981(4)	2.6(1)
N5	0.2033(7)	0.1394(3)	0.3429(4)	2.4(1)
N6	0.3981(7)	−0.1804(2)	0.4068(4)	2.2(1)
N7	0.3038(6)	−0.2069(2)	0.2187(4)	1.8(1)
N8	−0.0031(6)	−0.1911(3)	0.2330(4)	2.0(1)
N9	0.1011(7)	−0.1682(3)	0.4227(4)	2.4(1)
N10	0.1874(6)	−0.2648(2)	0.3495(4)	2.0(1)
C1	−0.0489(8)	0.0569(4)	0.3864(5)	3.0(2)
C2	−0.0983(9)	0.0381(4)	0.2838(6)	3.2(2)
C3	−0.017(1)	0.0407(4)	0.1311(6)	3.5(2)
C4	0.086(1)	0.0684(4)	0.0769(5)	3.6(2)
C5	0.250(1)	0.0535(3)	0.1144(5)	3.4(2)
C6	0.4726(9)	0.0646(4)	0.2476(6)	3.7(2)
C7	0.5174(9)	0.0823(4)	0.3531(6)	3.3(2)
C8	0.5103(9)	−0.2071(3)	0.3617(6)	3.0(2)
C9	0.4661(8)	−0.1928(4)	0.2563(5)	2.8(2)
C10	0.2445(9)	−0.1846(3)	0.1196(5)	2.7(2)
C11	0.0799(9)	−0.1994(4)	0.0819(5)	3.2(2)
C12	−0.0193(9)	−0.1685(3)	0.1330(5)	2.9(2)
C13	−0.1056(9)	−0.1604(4)	0.2835(6)	3.1(2)
C14	−0.0629(9)	−0.1779(4)	0.3882(6)	3.3(2)
C15	0.2227(7)	−0.0633(3)	0.3270(5)	1.9(1)

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)*[a^2*B(1,1)) + b^2*B(2,2) + c^2*B(3,3) + ab(\cos\gamma)*B(1,2) + ac(\cos\beta)*B(1,3) + bc(\cos\alpha)*B(2,3)]$.

TABLE III
Bond distances and angles for I.

(A) Bond distances in Angstroms

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Co1	N1	1.936(2)	Co1	N2	1.975(2)
Co1	N3	1.960(2)	Co1	N4	1.950(3)
Co1	N5	1.903(3)	Co1	O5	1.917(2)
Co2	N6	1.954(3)	Co2	N7	1.957(2)
Co2	N8	1.968(2)	Co2	N9	1.953(3)
Co2	N10	1.897(2)	Co2	O6	1.911(2)
O1	N5	1.229(3)	O2	N5	1.248(3)
O3	N10	1.236(3)	O4	N10	1.229(3)
O5	C15	1.291(3)	O6	C15	1.288(3)
O7	C15	1.277(3)	N1	C1	1.485(4)
N2	C2	1.481(4)	N2	C3	1.464(4)
N3	C5	1.477(4)	N3	C6	1.497(4)
N4	C7	1.457(4)	N6	C8	1.478(4)
N7	C9	1.496(4)	N7	C10	1.478(4)
N8	C12	1.490(4)	N8	C13	1.498(4)
N9	C14	1.486(4)	C1	C2	1.487(5)
C3	C4	1.506(5)	C4	C5	1.508(5)
C6	C7	1.513(5)	C8	C9	1.492(4)
C10	C11	1.519(4)	C11	C12	1.484(5)
C13	C14	1.503(5)			

(B) Bond angles in degrees

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
O5	Co1	N1	94.32(9)	O5	Co1	N2	86.6(1)
O5	Co1	N3	87.33(9)	O5	Co1	N4	90.5(1)
O5	Co1	N5	176.0(1)	N1	Co1	N2	86.1(1)
N1	Co1	N3	178.1(1)	N1	Co1	N4	93.1(1)
N1	Co1	N5	89.1(1)	N2	Co1	N3	95.0(1)
N2	Co1	N4	176.9(1)	N2	Co1	N5	91.5(1)
N3	Co1	N4	85.9(1)	N3	Co1	N5	89.3(1)
N4	Co1	N5	91.5(1)	O6	Co2	N6	90.8(1)
O6	Co2	N7	86.34(9)	O6	Co2	N8	88.3(1)
O6	Co2	N9	95.08(9)	O6	Co2	N10	175.4(1)
N6	Co2	N7	86.4(1)	N6	Co2	N8	178.1(1)
N6	Co2	N9	91.8(1)	N6	Co2	N10	91.4(1)
N7	Co2	N8	95.2(1)	N7	Co2	N9	177.8(1)
N7	Co2	N10	89.8(1)	N8	Co2	N9	86.6(1)
N8	Co2	N10	89.6(1)	N9	Co2	N10	88.9(1)
Co1	O5	C15	130.1(2)	Co1	N1	C1	109.5(2)
Co1	N2	C2	107.9(2)	Co1	N2	C3	117.6(2)
Co1	N2	H8	144.4(1)	Co1	N2	H9	104.4(1)
Co1	N3	C5	117.7(2)	Co1	N3	C6	107.3(2)
Co1	N4	C7	109.3(2)	Co1	N5	O1	122.5(2)
Co1	N5	O2	119.3(2)	Co2	O6	C15	129.9(2)
Co2	N6	C8	109.4(2)	Co2	N7	C9	107.9(2)
Co2	N7	C10	118.3(2)	Co2	N8	C12	115.9(2)
Co2	N8	C13	106.7(2)	Co2	N9	C14	109.5(2)

TABLE III (*cont.*)

(B) Bond angles in degrees

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
Co2	N10	O3	120.4(2)	Co2	N10	O4	121.5(2)
O1	N5	O2	118.1(3)	O3	N10	O4	118.2(3)
O5	C15	O6	114.8(2)	O5	C15	O7	121.7(3)
O6	C15	O7	123.4(3)	N1	C1	C2	107.0(3)
N2	C2	C1	107.9(3)	N2	C3	C4	111.9(3)
N3	C5	C4	110.7(3)	N3	C6	C7	107.1(3)
N4	C7	C6	104.8(3)	N6	C8	C9	106.8(3)
N7	C9	C8	108.4(3)	N7	C10	C11	111.2(3)
N8	C12	C11	111.0(3)	N8	C13	C14	107.2(3)
N9	C14	C13	106.7(3)	C2	N2	C3	113.1(3)
C5	N3	C6	110.6(3)	C9	N7	C10	111.6(3)
C12	N8	C13	110.7(3)	C3	C4	C5	114.5(3)
C10	C11	C12	113.1(3)				

(C) Hydrogen bonds (distances in Å, angles in °)

Intramolecular:				
O2-H7	2.210(2)	N2-H7.....O2	123.9(2)	
O3-H34	2.069(2)	N8-H34....O3	124.7(2)	
O7-H2	1.919(2)	N1-H2.....O7	143.3(2)	
O7-H39	1.988(2)	N9-H39....O7	142.3(2)	
Intermolecular:				
Cl1-Hw2	2.232(1)	Ow1-Hw2...Cl1	154.2(2)	Ow1 at $-x$, $-y$, $1-z$
Cl2-Hw4	2.250(1)	Ow2-Hw4...Cl2	179.1(2)	Ow2 at $1-x$, $-y$, $1-z$
O2-H27	2.027(2)	N7-H27....O2	149.6(2)	O2 at $1/2-x$, $-1/2+y$, $1/2-z$
O3-H14	2.217(2)	N3-H14....O3	144.4(2)	O3 at $1/2-x$, $1/2+y$, $1/2-z$

Numbers in parentheses are estimated standard deviations.

TABLE IV

Torsional angles (in degrees) for I.

Atom 1	Atom 2	Atom 3	Atom 4	Angle	Atom 1	Atom 2	Atom 3	Atom 4	Angle
N1	Co1	O5	C15	−29.3	N9	Co2	N7	C9	−51.8
N2	Co1	O5	C15	−115.1	N9	Co2	N7	C10	−179.6
N3	Co1	O5	C15	149.7	N10	Co2	N7	C9	−104.8
N4	Co1	O5	C15	63.8	N10	Co2	N7	C10	127.4
N5	Co1	O5	C15	−176.6	O6	Co2	N8	C12	46.8
O5	Co1	N1	C1	−100.2	O6	Co2	N8	C13	−77.0
N2	Co1	N1	C1	−13.9	N6	Co2	N8	C12	109.6
N3	Co1	N1	C1	110.5	N6	Co2	N8	C13	−14.2
N4	Co1	N1	C1	169.1	N7	Co2	N8	C12	−39.4
N5	Co1	N1	C1	77.6	N7	Co2	N8	C13	−163.1
O5	Co1	N2	C2	80.6	N9	Co2	N8	C12	142.0

TABLE IV (*cont.*)

Atom 1	Atom 2	Atom 3	Atom 4	Angle	Atom 1	Atom 2	Atom 3	Atom 4	Angle
O5	Co1	N2	C3	−48.9	N9	Co2	N8	C13	18.2
N1	Co1	N2	C2	−14.0	N10	Co2	N8	C12	−129.1
N1	Co1	N2	C3	−143.4	N10	Co2	N8	C13	107.1
N3	Co1	N2	C2	167.6	O6	Co2	N9	C14	98.5
N3	Co1	N2	C3	38.2	N6	Co2	N9	C14	−170.6
N4	Co1	N2	C2	59.9	N7	Co2	N9	C14	−132.2
N4	Co1	N2	C3	−69.5	N8	Co2	N9	C14	10.5
N5	Co1	N2	C2	−103.0	N10	Co2	N9	C14	−79.2
N5	Co1	N2	C3	127.6	O6	Co2	N10	O3	−40.0
O5	Co1	N3	C5	47.2	O6	Co2	N10	O4	138.5
O5	Co1	N3	C6	−78.3	N6	Co2	N10	O3	−159.0
N1	Co1	N3	C5	−163.4	N6	Co2	N10	O4	19.5
N1	Co1	N3	C6	71.1	N7	Co2	N10	O3	−72.6
N2	Co1	N3	C5	−39.2	N7	Co2	N10	O4	106.0
N2	Co1	N3	C6	−164.6	N8	Co2	N10	O3	22.6
N4	Co1	N3	C5	137.8	N8	Co2	N10	O4	−158.8
N4	Co1	N3	C6	12.4	N9	Co2	N10	O3	109.2
N5	Co1	N3	C5	−130.6	N9	Co2	N10	O4	−72.3
N5	Co1	N3	C6	104.0	Co1	O5	C15	O6	174.1
O5	Co1	N4	C7	105.6	Co1	O5	C15	O7	−3.3
N1	Co1	N4	C7	−160.0	Co2	O6	C15	O5	−174.4
N2	Co1	N4	C7	126.3	Co2	O6	C15	O7	2.9
N3	Co1	N4	C7	18.3	Co1	N1	C1	C2	38.8
N5	Co1	N4	C7	−70.9	Co1	N2	C2	C1	39.0
O5	Co1	N5	O1	−152.4	C3	N2	C2	C1	170.9
O5	Co1	N5	O2	26.5	Co1	N2	C3	C4	−54.9
N1	Co1	N5	O1	60.2	C2	N2	C3	C4	178.2
N1	Co1	N5	O2	−120.9	Co1	N3	C5	C4	56.7
N2	Co1	N5	O1	146.2	C6	N3	C5	C4	−179.5
N2	Co1	N5	O2	−34.8	Co1	N3	C6	C7	−39.7
N3	Co1	N5	O1	−118.8	C5	N3	C6	C7	−169.2
N3	Co1	N5	O2	60.2	Co1	N4	C7	C6	−43.9
N4	Co1	N5	O1	−32.9	Co2	N6	C8	C9	38.4
N4	Co1	N5	O2	146.1	Co2	N7	C9	C8	38.2
N6	Co2	O6	C15	−61.4	C10	N7	C9	C8	169.8
N7	Co2	O6	C15	−147.8	Co2	N7	C10	C11	−54.2
N8	Co2	O6	C15	116.9	C9	N7	C10	C11	179.7
N9	Co2	O6	C15	30.5	Co2	N8	C12	C11	59.4
N10	Co2	O6	C15	179.6	C13	N8	C12	C11	−179.0
O6	Co2	N6	C8	−100.4	Co2	N8	C13	C14	−43.1
N7	Co2	N6	C8	−14.1	C12	N8	C13	C14	−170.0
N8	Co2	N6	C8	−163.1	Co2	N9	C14	C13	−36.8
N9	Co2	N6	C8	164.5	N1	C1	C2	N2	−50.9
N10	Co2	N6	C8	75.6	N2	C3	C4	C5	68.7
O6	Co2	N7	C9	77.7	C3	C4	C5	N3	−69.2
O6	Co2	N7	C10	−50. 1	N3	C6	C7	N4	54.7
N6	Co2	N7	C9	−13.4	N6	C8	C9	N7	−50.2
N6	Co2	N7	C10	−141.2	N7	C10	C11	C12	69.2
N8	Co2	N7	C9	165.6	C10	C11	C12	N8	−72.5
N8	Co2	N7	C10	37.8	N8	C13	C14	N9	52.5

^{1}H and ^{13}C NMR Spectra

The ^{13}C nmr spectrum was recorded at room temperature in D_2O and referenced against the ^{13}C of TMS using a Nicolet NT-300 spectrometer equipped with a Tecmag Libra data station. Its trace is displayed in Figure 3. The chemical shifts of the resonances are given on the trace.

DISCUSSION

Prior to this study, we had prepared a number of related, mononuclear, derivatives of 2,3,2-tet and 3,2,3-tet and the characteristics of the unit cells of some of these substances are listed below.

Compound	*Space Group etc.*		
trans-[Co(3,2,3-tet)Cl_2]NO_3	$P2_1$ $M = 366.14$	$V = 739.59$ $d = 1.646$	$Z = 2$
trans-[Co(2,3,2-tet)$(NO_2)_2$]NO_3	$P2_1/n$ $M = 373.21$	$V = 1395.89$ $d = 1.776$	$Z = 4$
trans-[Co(3,2,3-tet)$(NO_2)_2$]Cl.3H_2O	$P2_12_12_1$ $M = 414.73$	$V = 1720.07$ $d = 1.601$	$Z = 4$

Since the volume and density of the unit cell of (I) are 2978.90 Å^3 and 1.599 gm cm^{-3}, respectively, it must either have 2 molecules in the asymmetric unit, or be a dimeric species. Therefore, we were not surprised when the latter alternative was found to be correct; however, we could not be sure of the nature of the bridge since nothing like it had been observed before, irrespective of whether the bridge was a μ-carbonato or a μ-nitrato fragment. Thus, simple tests such as the IR spectrum of (I) would not be an acceptable standard to differentiate between the several possibilities.

The presence of three waters of crystallization in the lattice seemed very clear from the elemental analysis and the X-ray structure; however, we could not find either of the hydrogens of one water, at least not at positions we were satisfied with. Therefore, what we called a water could, theoretically be an OH-anion, thus allowing for the presence of a μ-nitrato bridge. Finally, the carbon analysis was a little low, even if all the other analyses clearly pointed to its formulation as a μ-carbonato compound. Consequently, we resorted to nmr methods to distinguish between the two possibilities.

The four signals in the ^{13}C nmr spectrum nearest to TMS (32.9, 48.0, 53.1 and 59.8 ppm) are in the expected intensity ratio of 1:2:2:2 for the carbons of the 2,3,2-tet ligand. The presence of a ^{13}C resonance at 174.7 ppm (from TMS; which is the region of the ^{13}C signals reported for the –C=O– moieties of K[Co(EDTA)],[13] where the carbonyl ^{13}C resonances (TMS as standard) fell in the region of 182.4 to 185.9 ppm, while those of the –CH_2– fell in the region of 64.5 to 67.4 ppm) is significant. This is consistent with the spectrum shown in Figure 3, thus leaving no doubt that the bridging species is a carbonato ligand. This observation relieves us from further consideration that the bridge is an NO_3- ligand obtained from the oxidation of the NO_2- anions by hydrogen peroxide an equally attractive and intriguing possibility given the circumstances of the synthetic procedure and the known ability of certain metals to catalyze redox processes of small molecules.[14]

The molecule (see Fig. 1) can be visualized as two halves of composition [*trans*-Co(2,3,2-tet)(NO_2)], linked by a symmetrically disposed (μ-CO_3) bridge. The two five membered rings on each of the [*trans*-Co(2,3,2-tet)(NO_2)] fragments are inherently chiral, as expected; since they have opposite torsional angles (see below) the overall fragment is mesomeric insofar as the chiral properties of these rings are concerned. The central, six-membered ring is inherently mesomeric since the two chiral, secondary nitrogens are enantiomorphically related as a result of the need to orient the $-CH_2-CH_2-NH_2$ fragments in equatorial positions (*e.g.*, using the ranking order Co > C3 > C2 > N2 is (*R*), using the ranking order Co > C5 > C6, N3 is (*S*), using the ranking order Co > C10 > C9, N7 is (*R*)), and using the ranking order Co > C12 > C13, N8 is (*S*)).

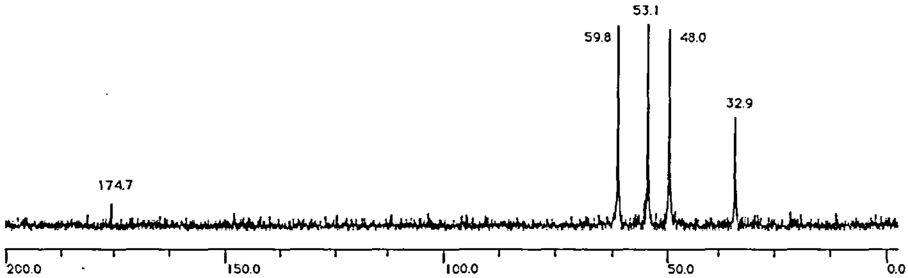


FIGURE 3 The ^{13}C nmr spectrum, referenced against TMS. The smallest peak, at 174.7 ppm, is due to the carbonato bridge (see text).

The arrangement of the two [*trans*-Co(2,3,2-tet)(NO_2)] halves is such that the molecule possesses a nearly perfect mirror plane passing through the C15–O7 vector of the [(μ-CO_3)] bridge. The chirality relationships are illustrated by the information tabulated below.

Fragment Chirality		*Torsional Angle*
N1–C1–C2–N2	−50.9	λ
N3–C6–C7–N4	+54.7	δ
N6–C8–C9–N7	−50.2	λ
N8–C13–C14–N9	+52.5	δ

The dispositions of these fragments are clear from Figure 1. Thus, the N1–C1–C2–N2 ligand(λ) can be mirrored into N8–C13–C14–N9(δ); the same observation applies to the N3–C6–C7–N4 and N6–C8–C9–N7 ligand fragments. Therefore, the molecule is mesomeric not only from the standpoint of the chiralities of the two *trans*-Co(2,3,2-tet)(NO_2) halves of the dimer, but from the internal chirality properties of the relevant fragments within each of the constituent halves.

As a result of the above observations, it is not surprising that the molecule crystallizes in a racemic space group, $P2_1/n$. The same remarks can be made concerning the closely related compound, [*trans*-Co(2,3,2-tet)$(NO_2)_2$]NO_3 (II) which shares with (I) a common [*trans*-Co(2,3,2-tet)(NO_2)] fragment. (II) crystallizes in the same racemic space group as (I) the most common of all the racemic space groups.[15]

The most significant hydrogen bonds formed in this molecule are those between the non-ligating oxygen of the carbonato bridge and the hydrogens of the adjacent primary amines from either half of the dimer (see Table III, part C). This is due not only to their strength (short distance and favourable bond angle) but also to their contribution to the stereochemistry of the species. By artificially inverting the positions of the atoms of one half of the dimer to give the rings formed by the 2,3,2-tet ligand the same conformations in both halves of the dimer, the minimum hydrogen bonding distance from the amine hydrogens of the inverted 2,3,2-tet ligand to the non-ligating oxygen of the carbonate increases from approximately 1.9 to 2.4 Å. Thus, despite the approximate nature of this estimate, an increase of this magnitude eliminates any additional stability that would be gained by such an isomer from the formation of this hydrogen bond, making a pair of homochiral ligands in the dimeric species an unfavourable prospect. There also exists an additional network of hydrogen bonds involving the secondary amine hydrogens and the nitro group oxygens that is similar to other metal amine complexes containing the same types of ligands.[16,17] Note that O2 and O3 are both locked into position by a pair of intramolecular and intermolecular hydrogen bonds. In the case of O2, the intermolecular hydrogen bond is stronger than the intramolecular hydrogen bond. In the case of O3, the situation is reversed. This arrangement is due to the nitro groups, which are free to rotate, accommodating the most favourable hydrogen bonds offered by the positioning of the amine hydrogens of each polyamine ligand.

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SUPPLEMENTARY MATERIAL

Fill lists of hydrogen positions, anisotropic thermal parameters, and observed and calculated structure factors are available from I.B.

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