Crystal Structure of the ω-Isomer of Chloro(diethylenetriamine)(ethylenediamine)cobalt(III) Dichloride Hemihydrate

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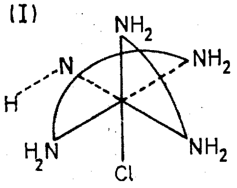
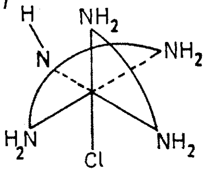
Crystals of title compound [isomer (IV)] are monoclinic, space group $C2$, with $Z = 4$, in a unit cell of dimensions $a = 14.323(1)$, $b = 7.720(1)$, $c = 12.229(1)$ Å, $\beta = 99.92(1)°$. The structure was solved from diffractometer data by Patterson and Fourier methods, and refined by full-matrix least-squares methods to R 0.045 for 2 416 reflections. The cobalt(III) ion is in octahedral co-ordination with the diethylenetriamine ligand adopting a facial (*cis*) configuration. The co-ordinated chloride ligand is *trans* to the NH group, and the ethylenediamine ligand occupies the remaining two co-ordination sites.

A NUMBER of chlorocobalt(III) complexes with ethylenediamine (en) and diethylenetriamine (dien) have been synthesized.[1-4] There are three distinct geometric isomers (II)—(IV) of the $[Co(en)(dien)Cl]^{2+}$ cation. In addition there are two different conformational isomers of isomer (I) [*i.e.* (I) and (II)], arising from the different configurations of the proton on the secondary nitrogen of the peripheral dien ligand. Bosnich and Dwyer[2] isolated initially only two isomers. The major product was named the ω-isomer and assigned configuration (III) or (IV), whilst the minor product was named the ε-isomer and assigned configuration (I) or (II). Gainsford and House[3] later claimed to have isolated all four isomers as their tetrachlorozincate salts, and assigned to them the configurations: (I) ω, (II) κ, (III) π, and (IV) ε, thus suggesting that Bosnich and Dwyer's ω-isomer[2] has configuration (I) rather than (III) or (IV). However, an initial single-crystal X-ray analysis of the dichloride hemihydrate salt of the ω-isomer, ω-$[Co(en)(dien)Cl]Cl_2,\frac{1}{2}H_2O$, by Johnston,[5] showed this isomer has the configuration (IV), in accord with the work of

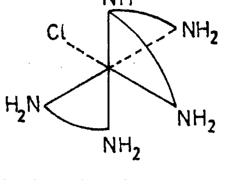
(I)



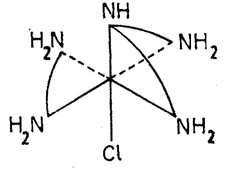
(II)



(III)



(IV)



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Bosnich and Dwyer.[2] At the same time Ablov *et al.*[6] also reported the preliminary results of a structural study of an unnamed isomer of anhydrous [Co(en)-(dien)Cl]Cl_2, which has the configuration of the ω-isomer reported here. However, no refinement was carried out and no atom parameters reported. Ensuing single-crystal *X*-ray structural determinations [7] showed the configurations assigned to the π and κ isomers by Gainsford and House [3] were correct. The assignments of these isomers, which we shall now use, are therefore: (II) κ, (III) π, and (IV) ω.

Later work by Gainsford and House [4] showed that the ε-isomer [thought to be (I)] had in fact not been isolated as reported earlier, but consisted of a 73–27% mixture of the π-[Co(en)(dien)Cl][$ZnCl_4$] and π-[Co(en)(dien)NO_2]-[$ZnCl_4$] isomers. Thus to date only the three geometrically distinct isomers (II)—(IV), and not the conformationally distinct isomers, have been isolated.

We now report the results of the refinement of the crystal structure of (IV), ω-[Co(en)(dien)Cl]Cl_2,$\frac{1}{2}H_2O$.

EXPERIMENTAL

Red prismatic crystals of ω-[Co(en)(dien)Cl]Cl_2,$\frac{1}{2}H_2O$ were prepared by the method of ref. 2.[8] One was cut to a cube of side *ca.* 0.1 m.

TABLE 1

Positional and anisotropic thermal parameters * with estimated standard deviations in parentheses

Atom	*x/a*	*y/b*	*z/c*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	0.2352(0)	0.0000	0.2978(0)	0.0019(0)	0.0066(1)	0.0024(0)	−0.0001(1)	0.0004(0)	−0.0002(1)
Cl	0.1294(0)	0.0012(4)	0.4152(1)	0.0027(0)	0.0109(1)	0.0037(0)	−0.0000(2)	0.0012(0)	0.0003(3)
Cl(1)	0.3617(1)	−0.0002(6)	0.6316(1)	0.0035(1)	0.0087(2)	0.0038(1)	0.0001(3)	0.0003(0)	−0.0000(3)
Cl(2)	0.2745(1)	0.0008(6)	0.9404(1)	0.0067(1)	0.0136(2)	0.0045(1)	−0.0007(4)	0.0018(1)	−0.0001(4)
N(1)	0.3348(2)	−0.006(1)	0.2066(2)	0.0027(1)	0.0110(6)	0.0033(1)	−0.0021(5)	0.0009(1)	0.0008(6)
N(2)	0.3076(4)	0.1811(8)	0.3844(5)	0.0027(3)	0.0082(9)	0.0031(4)	0.0010(4)	−0.0002(3)	−0.0025(5)
N(3)	0.1583(6)	0.174(1)	0.2065(7)	0.0045(4)	0.014(1)	0.0038(5)	−0.0011(6)	0.0005(4)	0.0029(6)
N(4)	0.1921(5)	0.3165(9)	0.6132(6)	0.0030(3)	0.010(1)	0.0049(5)	−0.0020(5)	0.0015(3)	0.0012(6)
N(5)	0.3407(4)	0.3267(8)	0.7968(6)	0.0023(3)	0.0073(9)	0.0040(4)	0.0020(4)	−0.0002(3)	−0.0005(5)
C(1)	0.4003(8)	0.214(2)	0.347(1)	0.0050(5)	0.016(2)	0.0096(9)	−0.0039(8)	0.0023(6)	−0.003(1)
C(2)	0.3926(7)	0.161(1)	0.2312(8)	0.0034(4)	0.010(1)	0.0048(6)	0.0003(6)	0.0005(4)	0.0018(7)
C(3)	0.1000(5)	0.292(1)	0.6476(6)	0.0020(3)	0.013(1)	0.0040(4)	−0.0009(5)	0.0007(3)	−0.0017(6)
C(4)	0.1120(6)	0.333(1)	0.7738(8)	0.0037(4)	0.015(2)	0.0062(7)	−0.0033(6)	0.0033(4)	−0.0011(8)
C(5)	0.4023(4)	0.3995(8)	0.8895(4)	0.0037(2)	0.0143(9)	0.0040(3)	−0.0006(4)	−0.0002(2)	0.0000(4)
C(6)	0.0695(4)	0.0751(7)	0.1482(5)	0.0034(2)	0.0131(8)	0.0055(4)	0.0008(4)	−0.0011(2)	−0.0003(5)
O	0.001(1)	0.545(1)	0.0311(8)	0.0106(8)	0.0209(8)	0.0139(6)	−0.0005(4)	0.0048(4)	−0.0040(4)

Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*
H(1) †	0.2786	−0.0030	0.1150	H(12)	0.3685	0.2766	0.1644
H(2)	0.2621	0.3116	0.3941	H(13)	0.4681	0.1588	0.1977
H(3)	0.3146	0.1621	0.4843	H(14)	0.4627	−0.1345	0.4073
H(4)	0.1419	0.2948	0.2541	H(15)	0.4353	−0.3429	0.3774
H(5)	0.1977	0.2485	0.1475	H(16)	0.4589	−0.1682	0.1908
H(6)	0.3123	−0.1665	0.4853	H(17)	0.3570	−0.2812	0.1683
H(7)	0.2642	−0.3153	0.3919	H(18)	0.1286	−0.0984	0.0296
H(8)	0.2062	−0.2981	0.1788	H(19)	0.0348	−0.1879	0.0741
H(9)	0.1201	−0.2804	0.2558	H(20)	0.0203	0.1566	0.0775
H(10)	0.4298	0.3568	0.3645	H(21)	0.0060	0.0712	0.2001
H(11)	0.4760	0.1571	0.4063				

* The temperature factor is of the form: $\exp - (h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkb_{12} + 2hlB_{13} + 2klB_{23})$. † *B* all 6.0 for H atoms.

Crystal Data.—$M = 337.6$, Monoclinic, $a = 14.323(1)$, $b = 7.720(1)$, $c = 12.229(1)$ Å, $\beta = 99.92(1)°$, $U = 1\,332$ Å^3, D_m(flotation) $= 1.68$ g cm^{-3}, $Z = 4$, $D_c = 1.68$ g cm^{-3}. Zr-filtered Mo-K_α radiation, $\lambda = 0.7107$ Å for intensity measurements, μ(Mo-K_α) = 19.3 cm^{-1}. Space group *C*2. Unit cell parameters and their estimated standard deviations were determined from a least squares fit of 12 reflections located by a peak search program on the Hilger and Watts diffractometer.

Intensity Measurements.—Intensity measurements were carried out by use of a Hilger and Watts four-circle *X*-ray diffractometer equipped with a scintillation counter, and a Philips PW 1010 *X*-ray generator. Four forms hkl, $\bar{h}kl$, $\bar{h}\bar{k}l$, and $h\bar{k}l$ were collected by a θ—ω step scan of 0.01° increments over the peaks. Intensities were assigned standard deviations according to standard statistics. The Friedel equivalent reflections were averaged, thereby yielding 2 490 independent reflections of which 2 112 were $> \sigma(I)$, and 1 923 $> 3\sigma(I)$. The intensities of three standard reflections measured every 75 reflections were within a 2σ tolerance throughout data collection, and hence only one scale factor was used in the refinement. Lorentz and polarization corrections, were applied but no corrections were made for absorption or extinction effects.

Solution and Refinement of the Structure.—The cobalt atom position was determined from a three-dimensional Patterson synthesis. Two cycles of isotropic refinement with the cobalt atom only gave *R* 0.53 for the 2 416 observable reflections. The three chlorine atoms were located from a subsequent Fourier map, and isotropic refinement of these four atoms gave *R* 0.316. From the next Fourier map the five nitrogen and six carbon atoms were located, and refinement of all atoms with anisotropic temperature factors for cobalt and three chlorine atoms, and isotropic temperature factors for carbon and nitrogen atoms, gave *R* 0.060. A difference Fourier map then showed a peak at (0.0020, 0.5337, 0.0198) which could possibly be attributed to the oxygen atom of the half molecule of water of crystal-

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lization associated with each asymmetric unit, as determined from analysis. However, as there are four asymmetric units per unit cell it was initially expected that this oxygen atom would lie on a two-fold symmetry axis with fractional co-ordinates (0, *y*, 0). The oxygen atom position was therefore introduced into the calculation as (0, 0.5337, 0), and the *y* co-ordinate and the isotropic temperature factor *B* refined, as well as the above-mentioned parameters for the other atoms. However, after four cycles of refinement the oxygen isotopic temperature factor had risen from 4.0 to 20.6 Å^2, thus suggesting this atom did not in fact lie on the two-fold axis. A subsequent refinement in which the *x*, *y*, and *z* co-ordinates, and *B* were refined for half an oxygen atom per asymmetric unit converged with *B* 6.19 and *R* 0.054. At this stage anisotropic temperature factors were applied to all atoms and a further refinement of two cycles gave *R* 0.050. The hydrogen atom positions were calculated from geometric considerations, assuming C–H and N–H 1.03 Å, and an isotropic temperature factor of 6.0 Å^2. Final anisotropic full-matrix non-hydrogen atom refinement converged, at *R* 0.045, and weighted *R′* 0.048, for the 2 416 observable reflections. The standard error in an observation of unit weight (see later) was 1.25. The hydrogen atom positions were recalculated and a final structure-factor calculation showed no change in the *R* and *R′*. A final difference-Fourier map showed no statistically observable peaks.

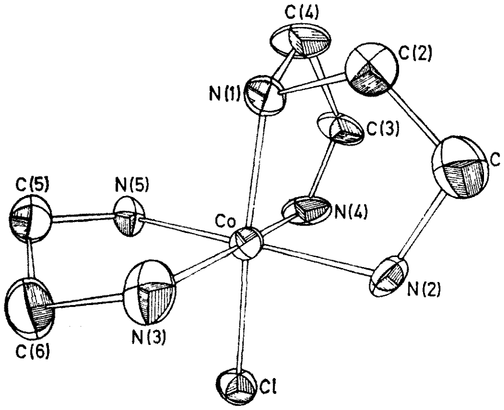
TABLE 2

Intramolecular bond lengths (Å) and bond angles (°), with estimated standard deviations in parentheses

(*a*) About Co			
(i) Lengths			
Co–N(1)	1.957(3)	Co–N(4)	1.971(7)
Co–N(2)	1.942(6)	Co–N(5)	1.969(6)
Co–N(3)	1.962(8)	Co–Cl	2.260(1)
(ii) Angles			
N(1)–Co–N(2)	87.4(3)	N(3)–Co–N(5)	86.2(1)
N(1)–Co–N(3)	94.9(3)	N(4)–Co–N(5)	91.3(3)
N(1)–Co–N(4)	86.0(3)	N(1)–Co–Cl	175.3(1)
N(1)–Co–N(5)	91.8(3)	N(2)–Co–Cl	90.2(2)
N(2)–Co–N(3)	90.6(3)	N(3)–Co–Cl	89.2(2)
N(2)–Co–N(4)	92.0(1)	N(4)–Co–Cl	90.0(2)
N(2)–Co–N(5)	176.6(3)	N(5)–Co–Cl	90.8(2)
N(3)–Co–N(4)	177.3(3)		
(*b*) About the ethylenediamine ring			
(i) Lengths			
N(3)–C(6)	1.549(9)	C(5)–C(6)	1.509(7)
N(5)–C(5)	1.426(8)		
(ii) Angles			
Co–N(3)–C(6)	104.9(5)	N(3)–C(6)–C(5)	110.1(5)
Co–N(5)–C(5)	113.7(4)	N(5)–C(5)–C(6)	105.8(5)
(*c*) About the diethylenetriamine ring			
(i) Lengths			
N(1)–C(2)	1.531(12)	N(4)–C(3)	1.465(9)
N(1)–C(4)	1.454(12)	C(1)–C(2)	1.457(16)
N(2)–C(1)	1.502(12)	C(3)–C(4)	1.557(12)
(ii) Angles			
Co–N(1)–C(2)	106.9(6)	N(1)–C(2)–C(1)	112.2(7)
Co–N(1)–C(4)	109.8(5)	N(1)–C(4)–C(3)	107.8(6)
Co–N(2)–C(1)	111.9(6)	N(2)–C(1)–C(2)	109.0(8)
Co–N(4)–C(3)	110.6(5)	N(4)–C(3)–C(4)	107.8(6)
C(2)–N(1)–C(4)	115.8(3)		

All computations were performed on a Burroughs B 6700 computer using the Canterbury University suite of *X*-ray-crystallographic programs.[9] All refinements were by full-matrix least-squares methods, the quantity minimized being $\Sigma w(F_o - F_c)^2$, where $w = 4F_o^2/\sigma^2(F_c^2)$. The standard error in an observation of unit weight was $[\Sigma w(F_o - F_c)^2/(N_O - N_V)]^{\frac{1}{2}}$ for N_O observable reflections and N_V parameters. Atomic scattering factors were taken from ref. 10.

Final atomic parameters, with their estimated standard deviations, are shown in Table 1, and bond lengths and bond angles in Table 2. The molecule is shown diagrammatically in the Figure. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21355 (6 pp., 1 microfiche).*



General view of the ω-[Co(en)(dien)Cl]$^{2+}$ cation

DISCUSSION

The crystal structure consists of four ω-[Co(en)(dien)Cl]Cl_2 molecules in the unit cell, with two water molecules statistically distributed over four positions near the two-fold axes of the unit cell.

The cobalt atom is in octahedral co-ordination with the terdentate dien ligand in a facial (*cis*) configuration and the co-ordinated chlorine is *trans* to the secondary nitrogen of this dien ligand. The en ligand is bidentate, and completes the co-ordination sphere [configuration (IV)].

The angles around the central cobalt atom are all close to, yet significantly different from, 90°, indicating that the co-ordination sphere is slightly distorted from octahedral symmetry. The three Co–N bond distances of the dien ring are statistically different, whereas those of the en ring are statistically equivalent indicating a greater degree of distortion in the former ring. The mean Co–N distance for the dien ring [1.957(5) Å] is however equivalent to that [1.966(7) Å] for the en ring. A parallel situation exists for the π-isomer [dien ring, 1.970(7), en ring, 1.966(7) Å)] and the κ-isomer[7] [dien ring, 1.96(1); en ring, 1.96(1) Å]. These mean Co–N bond distances are comparable to those of related complexes.[11-13]

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue (items less than 10 pp. are supplied as full-size copies).

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Both the en and dien rings have a typical gauche configuration. The N(5)–Co–N(3) angle of the en ring [86.2(1)°] is close to the N(1)–Co–N(2) [87.4(3)°] and N(1)–Co–N(4) [86.0(3)°] angles of the dien ring. These agree well with the corresponding values for the π-isomer[7] [en ring, 85.7(3)°; dien ring, 87.2(3)° and 87.3(3)°], but are generally significantly larger than those for the κ-isomer[7] [en ring, 85.1(5)°; dien ring, 85.6(6)° and 84.9(5)°]. This indicates a greater degree of angular ring strain when the dien ligand is co-ordinated in peripheral, rather than a facial (*cis*) configuration. However the significant difference in the C–C bond lengths of the dien ring [1.457(16) and 1.557(12) Å] show some distortion is present in such a facial configuration of the dien ligand. A similar effect is shown by the π-isomer. This effect is not shown by the κ-isomer[7] as in this situation the dien ligand is co-ordinated in a near-symmetrical orientation with respect to the en ligand.

The angles within the rings all approach the ideal tetrahedral angle, with the notable exception of C(2)–N(1)–C(4) angle [115.8(3)°] about the secondary nitrogen of the dien ring. This angular distortion is common in both facially and peripherally co-ordinated dien and trien ligands.[7,13,14]

The Co–Cl distance [2.260(1) Å] lies in the range of other such similar determinations.[7,15,16] The oxygen of the water molecule lies 3.17 Å from the ionic chloride (Table 1) thus suggesting that the water is hydrogen bonded to it.

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