Preparation and Crystal and Molecular Structure of [1-Chloro-2,2-bis-(*p*-chlorophenyl)vinyl]bis(dimethylglyoximato)pyridinecobalt(III)

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Crystals of the title compound, produced by reaction of bis(dimethylglyoximato)pyridinecobalt(I) with 1,1-bis-(*p*-chlorophenyl)-2,2,2-trichloroethane (*p,p'*-DDT), are orthorhombic, space group $Pn2_1a$, a = 25.50(2), b = 23.13(2), c = 9.728(7) Å, Z = 8. The structure was solved by Patterson superposition methods from two-circle diffractometer data, and refined to R 0.048 for 3 545 unique observed reflections. The asymmetric unit consists of two molecules, each with octahedral co-ordination of cobalt, which differ significantly only in the relative orientations of the aromatic rings and the effect this has on the bis(dimethylglyoximato) plane. A chlorovinyl group is σ-bonded to cobalt, with mean bond lengths: Co–C 1.970(13), C=C 1.366(15), and C–Cl 1.803(13) Å, mean Co–N distances are 2.042(10) (pyridine) and 1.877(10) Å (oxime). The symmetry of the crystallographically independent O–H · · · O hydrogen bonds [O · · · O (mean) 2.50(1) Å] is discussed. This σ-vinyl derivative may be relevant to the degradation of DDT in biological systems.

THE title compound has been synthesised, and the molecular structure determined by single-crystal *X*-ray diffraction, as part of an investigation of the possible involvement of alkylcobalt species in the biological reactions of the insecticide DDT.[1] A preliminary account has appeared.[2]

EXPERIMENTAL

1,1-Bis(*p*-chlorophenyl)-2,2,2-trichloroethane (1.77 g, 5 mmol) in methanol (80 ml) was added to a solution of bis-(dimethylglyoximato)pyridinecobalt(I) (5 mmol) produced under nitrogen in methanol (50 ml) by the literature method.[3] The solution was warmed to 40 °C and stirred for 3 h in the dark. A yellow-orange *product* (1.8 g, 55%) precipitated. T.l.c. of the precipitate (silica plate developed with acetone) showed the presence of a single compound with R_F 0.66. Crystals suitable for *X*-ray diffraction were grown from methanol (Found: C, 49.9; H, 4.2; N, 11.0. Calc. for $C_{27}H_{27}N_5Cl_3O_4Co$: C, 49.8; H, 4.2; N, 10.8%).

Intensities were determined on a Stoe Stadi-2 two-circle diffractometer for two crystals (layers 0—23*kl* and *hk*0—6) of dimensions *ca.* 0.49 × 0.14 × 0.04 and 0.49 × 0.12 × 0.05 mm, by use of Mo-K_α radiation and a graphite crystal monochromator. Data were collected in an approximately ' constant count ' mode; where a prescan indicated that the preset count could not be achieved within a specified time, the reflection was ignored. As tationary-background–ω scan–stationary-background technique was employed, with variable reflection width, and with the background-measurement time proportional to the step-measurement time. Of the 7 071 reflections measured, 301 were rejected, mainly because of background imbalance or because the net count was $<2.5\ \sigma$, based on counting statistics. Interlayer scale factors were calculated from common reflections by a linear least-squares method. Averaging equivalent reflections led to 3 545 unique observed reflections. Lorentz, polarisation, and absorption corrections were applied. Unit-cell dimensions were obtained by a least-squares fit to the diffractometer ω angle measurements.

RESULTS

Crystal Data.—$C_{27}H_{27}Cl_3CoN_5O_4$, $M = 650.8$, Orthorhombic, $a = 25.50(2)$, $b = 23.13(2)$, $c = 9.728(7)$ Å, D_m (flotation) = 1.48 $Z = 8$, $D_c = 1.51$ g cm^{-3}, $U = 5\,738$ Å^3, $F(000) = 2\,672$. Mo-K_α radiation, $\lambda = 0.71069$ Å; μ(Mo-K_α) = 8.6 cm^{-1}. Space group *Pnma* or $Pn2_1a$ from systematic absences: 0*kl* with $k + l$ odd, *hk*0 with *h* odd.

Structure Solution and Refinement.—After attempts to solve the structure by direct methods had been unsuccessful in both possible space groups, the Patterson function was interpreted to give the co-ordinates of two cobalt atoms in the non-centrosymmetric $Pn2_1a$. We were unable to interpret a difference electron-density synthesis phased by these two atoms, but an eight-fold Patterson superposition minimum function derived from the cobalt atoms and their symmetry equivalents yielded co-ordinates for several other atoms. The remaining atoms, including most of the hydrogen atoms, were located in successive difference electron-density syntheses. Since the structure was too large to refine by full-matrix least-squares with our computing facilities, a novel version of the conjugate-gradient method was employed for the initial refinement cycles;[4] finally each of the two molecules was refined independently for two cycles of full-matrix least-squares. The full covariance matrices were employed in estimating the standard deviations in bond lengths and angles (which also include contributions from the estimated errors in unit-cell parameters), so these should be close to the values which would have been obtained by an overall full-matrix method. Anisotropic temperature factors were employed for the cobalt and chlorine atoms, with isotropic temperature factors for the remaining atoms. Groups of chemically similar hydrogen atoms in the same molecule were assigned common variable-temperature factors. Complex neutral-atom scattering factors were employed for carbon, nitrogen, oxygen, and chlorine,[5,6] together with a complex cobalt(II) scattering factor [5,6] and a bonded hydrogen-atom scattering factor.[7]

The hydrogen atoms attached to the aromatic rings were inserted in calculated positions on the external bisectors of

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[1] R. H. Prince and D. A. Stotter, *Nature*, 1974, **249**, 286.

[2] R. H. Prince, G. M. Sheldrick, D. A. Stotter, and R. Taylor, *J.C.S. Chem. Comm.*, 1974, 854.

[3] G. N. Schrauzer and R. J. Windgassen, *J. Amer. Chem. Soc.*, 1966, **88**, 3738.

[4] G. M. Sheldrick, unpublished work.

[5] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[6] D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.

[7] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

the C–C–C angles with C–H 1.08 Å, and refined subject to the constraint that the C–H vectors remained constant in magnitude and direction while the carbon atoms were free to move. The methyl groups were refined as rigid groups with C–H 1.08 Å, and H–C–H 109.5°. The hydrogen-bonded hydrogen atoms were allowed to refine independently.

Refinement with the opposite polar axis direction from that given here produced a significantly higher generalised *R* index, but there was no change on reversing the relative

TABLE 1

Atom co-ordinates ($\times 10^4$) and isotropic vibrational amplitudes ($Å^2 \times 10^3$)

	x/*a*	*y*/*b*	*z*/*c*	*B*/Å²		*x*/*a*	*y*/*b*	*z*/*c*	*B*/Å²
Co(1)	42(1)	−2	1 403(2)		Co(2)	2 595	2 500(1)	1 063(2)	
Cl(1)	274(1)	412(1)	4 464(3)		Cl(1′)	2 503(1)	2 035(1)	4 134(3)	
Cl(2)	−761(2)	2 929(2)	−1 376(4)		Cl(2′)	3 623(2)	−200(1)	−2 186(4)	
Cl(3)	957(2)	2 720(2)	7 161(4)		Cl(3′)	1 855(2)	−369(2)	6 533(4)	
O(1)	1 082(3)	255(3)	470(8)	58(2)	O(1′)	1 638(3)	2 005(3)	75(8)	56(2)
O(2)	−917(3)	430(3)	381(8)	52(2)	O(2′)	3 633(3)	2 311(3)	30(9)	53(2)
O(3)	−977(3)	−207(3)	2 458(8)	57(2)	O(3′)	3 563(3)	2 960(3)	2 083(9)	56(2)
O(4)	1 002(3)	−511(3)	2 269(8)	56(2)	O(4′)	1 565(3)	2 708(3)	2 013(8)	48(2)
H(1)	1 079(27)	−184(32)	1 650(80)	22(15)	H(1′)	1 532(28)	2 376(35)	1 045(87)	30(15)
H(2)	−968(27)	123(30)	1 433(85)	22(15)	H(2′)	3 611(28)	2 590(34)	963(89)	30(15)
N(1)	555(3)	338(4)	298(10)	47(3)	N(1′)	2 158(3)	2 073(3)	−121(9)	35(2)
C(2)	396(4)	640(4)	−776(12)	45(3)	C(2′)	2 383(4)	1 844(4)	−1 192(12)	42(3)
C(3)	758(5)	892(6)	−1 839(14)	74(4)	C(3′)	2 098(5)	1 552(5)	−2 332(13)	57(4)
H(3a)	568(5)	1 102(6)	−2 697(14)	146(20)	H(3a′)	2 302(5)	1 590(5)	−3 300(13)	141(21)
H(3b)	1 021(5)	563(6)	−2 215(14)	146(20)	H(3b′)	1 689(5)	1 660(5)	−2 476(13)	141(21)
H(3c)	976(5)	1 208(6)	−1 256(14)	146(20)	H(3c′)	2 130(5)	1 114(5)	−1 957(13)	141(21)
C(4)	−174(4)	674(4)	−803(11)	39(3)	C(4′)	2 948(4)	1 939(5)	−1 206(13)	46(3)
C(5)	−470(5)	979(5)	−1 921(14)	63(4)	C(5′)	3 286(5)	1 751(5)	−2 361(14)	69(4)
H(5a)	−245(5)	1 221(5)	−2 664(14)	146(20)	H(5a′)	3 029(5)	1 480(5)	−2 965(14)	141(21)
H(5b)	−663(5)	1 275(5)	−1 227(14)	146(20)	H(5b′)	3 587(5)	1 487(5)	−1 897(14)	141(21)
H(5c)	−761(5)	722(5)	−2 447(14)	146(20)	H(5c′)	3 465(5)	2 071(5)	−3 018(14)	141(21)
N(6)	−396(3)	433(4)	260(9)	39(2)	N(6′)	3 109(3)	2 205(3)	−133(9)	31(2)
N(7)	−458(3)	−358(3)	2 529(9)	39(2)	N(7′)	3 030(3)	2 963(3)	2 195(10)	43(2)
C(8)	−291(4)	−714(5)	3 416(12)	44(3)	C(8′)	2 787(5)	3 273(5)	3 115(12)	47(3)
C(9)	−641(5)	−972(6)	4 515(14)	75(4)	C(9′)	3 098(5)	3 605(5)	4 142(14)	70(4)
H(9a)	−444(5)	−1 324(6)	5 028(14)	146(20)	H(9a′)	2 852(5)	3 929(5)	4 613(14)	141(21)
H(9b)	−1 009(5)	−1 122(6)	4 099(14)	146(20)	H(9b′)	3 407(5)	3 813(5)	3 566(14)	141(21)
H(9c)	− 713(5)	−628(6)	5 241(14)	146(20)	H(9c′)	3 268(5)	3 335(5)	4 931(14)	141(21)
C(10)	254(4)	−805(5)	3 371(12)	45(3)	C(10′)	2 228(4)	3 200(5)	3 118(12)	43(3)
C(11)	546(5)	−1 170(5)	4 357(14)	66(4)	C(11′)	1 865(5)	3 452(5)	4 145(14)	71(4)
H(11a)	282(5)	−1 413(5)	5 005(14)	146(20)	H(11a′)	2 096(5)	3 777(5)	4 660(14)	141(21)
H(11b)	853(5)	−983(5)	4 979(14)	146(20)	H(11b′)	1 678(5)	3 178(5)	4 899(14)	141(21)
H(11c)	717(5)	−1 454(5)	3 599(14)	146(20)	H(11c′)	1 569(5)	3 659(5)	3 521(14)	141(21)
N(12)	481(3)	−495(4)	2 435(9)	43(3)	N(12′)	2 076(3)	2 834(3)	2 150(10)	44(3)
N(13)	−34(3)	−656(3)	0(9)	34(2)	N(13′)	2 509(3)	3 173(3)	−273(9)	37(2)
C(14)	386(4)	−877(5)	−630(12)	50(3)	C(14′)	2 037(4)	3 361(5)	−654(11)	47(3)
H(14)	772(4)	−718(5)	−373(12)	118(13)	H(14′)	1 693(4)	3 158(5)	−223(11)	108(12)
C(15)	332(5)	−1 320(5)	−1 634(13)	61(4)	C(15′)	1 970(5)	3 822(5)	−1 617(12)	51(3)
H(15)	673(5)	−1 476(5)	−2 180(13)	118(13)	H(15′)	1 584(5)	3 971(5)	−1 906(12)	108(12)
C(16)	−140(4)	−1 544(6)	−1 904(13)	53(3)	C(16′)	2 410(5)	4 067(5)	−2 152(13)	60(3)
H(16)	−182(4)	−1 890(5)	−2 643(13)	118(13)	H(16′)	2 375(5)	4 421(5)	−2 869(13)	108(12)
C(17)	−568(5)	−1 330(5)	−1 235(13)	63(4)	C(17′)	2 902(5)	3 868(5)	−1 794(14)	67(4)
H(17)	−954(5)	−1 503(5)	−1 438(13)	118(13)	H(17′)	3 253(5)	4 053(5)	−2 230(14)	108(12)
C(18)	−500(4)	−877(5)	−265(12)	49(3)	C(18′)	2 926(5)	3 418(5)	−844(12)	51(3)
H(18)	−839(4)	−709(5)	268(12)	118(13)	H(18′)	3 308(5)	3 258(5)	−554(12)	108(12)
C(19)	111(4)	634(5)	2 738(13)	52(3)	C(19′)	2 635(4)	1 851(5)	2 369(12)	48(3)
C(20)	75(4)	1 228(5)	2 661(12)	51(3)	C(20′)	2 645(4)	1 271(4)	2 190(11)	40(3)
C(21)	−126(4)	1 578(4)	1 527(12)	44(3)	C(21′)	2 857(4)	932(4)	981(11)	39(3)
C(22)	−654(5)	1 668(5)	1 418(13)	59(4)	C(22′)	3 390(4)	949(5)	833(12)	51(3)
H(22)	−914(5)	1 415(5)	2 055(13)	118(13)	H(22′)	3 624(4)	1 239(5)	1 451(12)	108(12)
C(23)	−871(5)	2 068(6)	516(14)	72(4)	C(23′)	3 635(5)	573(5)	−161(13)	68(4)
H(23)	−1 290(5)	2 123(6)	437(14)	118(13)	H(23′)	4 056(5)	565(5)	−283(13)	108(12)
C(24)	−519(5)	2 405(6)	−303(14)	77(4)	C(24′)	3 332(4)	241(4)	−919(12)	47(3)
C(25)	−1(5)	2 318(5)	−209(13)	59(4)	C(25′)	2 809(5)	218(5)	−787(12)	58(4)
H(25)	257(5)	2 559(5)	−876(13)	118(13)	H(25′)	2 580(5)	−66(5)	−1 431(12)	108(12)
C(26)	219(5)	1 917(5)	736(13)	68(4)	C(26′)	2 558(5)	580(5)	224(12)	53(3)
H(26)	639(5)	1 874(5)	842(13)	118(13)	H(26′)	2 138(5)	566(5)	365(12)	108(12)
C(27)	283(4)	1 595(4)	3 779(12)	42(3)	C(27′)	2 463(4)	851(4)	3 324(11)	39(3)
C(28)	−54(5)	1 894(5)	4 756(13)	59(4)	C(28′)	2 799(5)	623(5)	4 243(12)	53(3)
H(28)	−474(5)	1 850(5)	4 670(13)	118(13)	H(28′)	3 208(5)	742(5)	4 204(12)	108(12)
C(29)	149(5)	2 224(5)	5 761(14)	62(4)	C(29′)	2 631(5)	240(5)	5 231(13)	59(4)
H(29)	−105(5)	2 422(5)	6 514(14)	118(13)	H(29′)	2 901(5)	47(5)	5 951(13)	108(12)
C(30)	681(5)	2 306(4)	5 823(12)	53(3)	C(30′)	2 108(4)	114(4)	5 261(11)	45(3)
C(31)	1 018(5)	2 035(5)	4 935(14)	67(4)	C(31′)	1 747(5)	310(5)	4 368(13)	65(4)
H(31)	1 437(5)	2 083(5)	5 046(14)	118(13)	H(31′)	1 342(5)	176(5)	4 415(13)	108(12)
C(32)	806(5)	1 697(5)	3 886(13)	59(3)	C(32′)	1 935(5)	712(5)	3 345(12)	55(3)
H(32)	1 067(5)	1 511(5)	3 132(13)	118(13)	H(32′)	1 668(5)	898(5)	2 605(12)	108(12)

hand with which the data from the two crystals were combined. The weighting scheme was $w = \Sigma[\sigma^2(N) + 0.001N^2]^{-1}/[19.84 + |F_o| + 0.00327\ F_o^2]$, where N is the net peak count, and the summation is over equivalent reflections. An analysis of variance showed that the mean values of $w\Delta^2$ were virtually independent of the magnitudes of F_o and $\sin\theta$. The refinement converged to R' 0.050 [$= \Sigma w\Delta/\Sigma w|F_o|$ where $\Delta = |F_o - F_c|$], with a corresponding unweighted R index of 0.048. The highest peak in the final electron-density synthesis was *ca.* 0.8 eÅ^{-3}. Atom co-ordinates and temperature factors are given in Tables 1 and 2, the resulting bond lengths and angles in Tables 3 and 4. Some short non-bonded distances are given in Table 5. Observed and calculated structure factors are

TABLE 2

Anisotropic * vibrational amplitudes ($Å^2 \times 10^3$)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co(1)	37(1)	39(1)	41(1)	5(1)	0(1)	1(1)
Cl(1)	94(3)	51(2)	47(2)	−2(2)	−13(2)	−3(2)
Cl(2)	223(5)	56(2)	61(3)	9(2)	−14(3)	29(3)
Cl(3)	127(3)	82(3)	66(3)	−11(2)	−9(3)	−36(2)
Co(2)	38(1)	39(1)	37(1)	2(1)	3(1)	3(1)
Cl(1′)	100(3)	50(2)	40(2)	10(2)	10(2)	9(2)
Cl(2′)	130(3)	61(2)	55(2)	−8(2)	4(2)	25(2)
Cl(3′)	200(5)	81(3)	70(3)	26(2)	−2(3)	−60(3)

* In the form: $-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)$.

TABLE 3

Bond lengths (Å)

Co(1)–N(1)	1.867(10)	Co(2)–N(1′)	1.884(10)
Co(1)–N(6)	1.871(9)	Co(2)–N(6′)	1.879(10)
Co(1)–N(7)	1.871(9)	Co(2)–N(7′)	1.894(11)
Co(1)–N(12)	1.886(10)	Co(2)–N(12′)	1.861(10)
Co(1)–N(13)	2.046(10)	Co(2)–N(13′)	2.039(10)
Co(1)–C(19)	1.971(13)	Co(2)–C(19′)	1.968(13)
O(1)–H(1)	1.534(86)	O(1′)–H(1′)	1.304(88)
O(4)–H(1)	0.986(77)	O(4′)–H(1′)	1.219(88)
O(2)–H(2)	1.253(82)	O(2′)–H(2′)	1.115(88)
O(3)–H(2)	1.255(81)	O(3′)–H(2′)	1.389(88)
O(1)–N(1)	1.368(11)	O(1′)–N(1′)	1.348(10)
N(1)–C(2)	1.321(13)	N(1′)–C(2′)	1.303(13)
C(2)–C(3)	1.503(16)	C(2′)–C(3′)	1.488(16)
C(2)–C(4)	1.454(15)	C(2′)–C(4′)	1.457(15)
C(4)–C(5)	1.501(15)	C(4′)–C(5′)	1.482(16)
C(4)–N(6)	1.305(13)	C(4′)–N(6′)	1.280(13)
O(2)–N(6)	1.334(10)	O(2′)–N(6′)	1.368(11)
O(3)–N(7)	1.372(11)	O(3′)–N(7′)	1.362(11)
N(7)–C(8)	1.267(13)	N(7′)–C(8′)	1.305(13)
C(8)–C(9)	1.515(17)	C(8′)–C(9′)	1.488(16)
C(8)–C(10)	1.405(15)	C(8′)–C(10′)	1.435(16)
C(10)–C(11)	1.479(16)	C(10′)–C(11′)	1.481(16)
C(10)–N(12)	1.296(13)	C(10′)–N(12′)	1.326(13)
O(4)–N(12)	1.338(11)	O(4′)–N(12′)	1.343(11)
N(13)–C(18)	1.320(13)	N(13′)–C(18′)	1.327(13)
N(13)–C(14)	1.336(13)	N(13′)–C(14′)	1.331(13)
C(14)–C(15)	1.422(16)	C(14′)–C(15′)	1.430(15)
C(15)–C(16)	1.336(16)	C(15′)–C(16′)	1.362(15)
C(16)–C(17)	1.365(16)	C(16′)–C(17′)	1.381(16)
C(17)–C(18)	1.420(16)	C(17′)–C(18′)	1.393(16)
Cl(1)–C(19)	1.805(13)	Cl(1′)–C(19′)	1.801(13)
C(19)–C(20)	1.378(15)	C(19′)–C(20′)	1.354(14)
C(20)–C(21)	1.461(16)	C(20′)–C(21′)	1.512(15)
C(21)–C(26)	1.407(16)	C(21′)–C(26′)	1.337(14)
C(21)–C(22)	1.366(15)	C(21′)–C(22′)	1.367(15)
C(22)–C(23)	1.391(17)	C(22′)–C(23′)	1.444(16)
C(23)–C(24)	1.431(18)	C(23′)–C(24′)	1.315(15)
C(24)–C(25)	1.337(17)	C(24′)–C(25′)	1.339(16)
C(25)–C(26)	1.422(17)	C(25′)–C(26′)	1.442(15)
Cl(2)–C(24)	1.716(15)	Cl(2′)–C(24′)	1.764(12)
C(20)–C(27)	1.478(15)	C(20′)–C(27′)	1.542(15)
C(27)–C(32)	1.358(15)	C(27′)–C(32′)	1.385(15)
C(27)–C(28)	1.457(16)	C(27′)–C(28′)	1.346(14)
C(28)–C(29)	1.343(16)	C(28′)–C(29′)	1.375(15)
C(29)–C(30)	1.371(16)	C(29′)–C(30′)	1.365(15)
C(30)–C(31)	1.371(16)	C(30′)–C(31′)	1.344(15)
C(31)–C(32)	1.394(16)	C(31′)–C(32′)	1.443(16)
Cl(3)–C(30)	1.764(13)	Cl(3′)–C(30′)	1.788(12)

TABLE 4

Bond angles (°)

N(6)–Co(1)–N(1)	81.3(5)	N(6′)–Co(2)–N(1′)	81.0(5)
N(12)–Co(1)–N(1)	98.4(5)	N(12′)–Co(2)–N(1′)	98.2(5)
N(13)–Co(1)–N(1)	89.6(5)	N(13′)–Co(2)–N(1′)	86.9(4)
C(19)–Co(1)–N(1)	90.1(5)	C(19′)–Co(2)–N(1′)	91.5(5)
N(7)–Co(1)–N(6)	100.2(5)	N(7′)–Co(2)–N(6′)	99.0(5)
N(13)–Co(1)–N(6)	86.9(4)	N(13′)–Co(2)–N(6′)	87.5(4)
C(19)–Co(1)–N(6)	92.4(5)	C(19′)–Co(2)–N(6′)	95.0(5)
N(13)–Co(1)–N(7)	90.1(4)	N(13′)–Co(2)–N(7′)	90.2(4)
N(12)–Co(1)–N(7)	80.1(5)	N(12′)–Co(2)–N(7′)	81.5(5)
C(19)–Co(1)–N(7)	90.2(5)	C(19′)–Co(2)–N(7′)	91.5(5)
C(19)–Co(1)–N(12)	92.8(5)	C(19′)–Co(2)–N(12′)	89.2(5)
N(7)–Co(1)–N(1)	178.4(4)	N(7′)–Co(2)–N(1′)	177.1(4)
N(12)–Co(1)–N(6)	174.8(4)	N(12′)–Co(2)–N(6′)	175.7(4)
C(19)–Co(1)–N(13)	179.2(4)	C(19′)–Co(2)–N(13′)	176.7(4)
N(13)–Co(1)–N(12)	88.0(4)	N(13′)–Co(2)–N(12′)	88.2(5)
N(1)–O(1)–H(1)	100.2(32)	N(1′)–O(1′)–H(1′)	103.2(33)
N(6)–O(2)–H(2)	100.3(33)	N(6′)–O(2′)–H(2′)	98.6(39)
N(7)–O(3)–H(2)	100.1(33)	N(7′)–O(3′)–H(2′)	98.9(31)
N(12)–O(4)–H(1)	104.5(43)	N(12′)–O(4′)–H(1′)	106.2(36)
O(1)–H(1)–O(4)	164.9(65)	O(1′)–H(1′)–O(4′)	163.8(65)
O(3)–H(2)–O(2)	174.6(63)	O(3′)–H(2′)–O(2′)	176.5(68)
O(1)–N(1)–Co(1)	124.0(7)	O(1′)–N(1′)–Co(2)	123.9(7)
C(2)–N(1)–Co(1)	117.6(8)	C(2′)–N(1′)–Co(2)	116.2(8)
C(2)–N(1)–O(1)	118.2(9)	C(2′)–N(1′)–O(1′)	120.0(9)
C(3)–C(2)–N(1)	124.0(10)	C(3′)–C(2′)–N(1′)	124.4(10)
C(4)–C(2)–N(1)	110.5(11)	C(4′)–C(2′)–N(1′)	112.5(11)
C(4)–C(2)–C(3)	125.4(11)	C(4′)–C(2′)–C(3′)	123.0(11)
C(5)–C(4)–C(2)	122.8(10)	C(5′)–C(4′)–C(2′)	122.5(11)
N(6)–C(4)–C(2)	113.3(11)	N(6′)–C(4′)–C(2′)	112.4(11)
N(6)–C(4)–C(5)	123.8(9)	N(6′)–C(4′)–C(5′)	125.0(10)
O(2)–N(6)–Co(1)	122.6(7)	O(2′)–N(6′)–Co(2)	122.9(6)
C(4)–N(6)–Co(1)	116.2(8)	C(4′)–N(6′)–Co(2)	117.2(8)
C(4)–N(6)–O(2)	120.3(9)	C(4′)–N(6′)–O(2′)	119.6(9)
O(3)–N(7)–Co(1)	121.2(7)	C(3′)–N(7′)–Co(2)	122.3(7)
C(8)–N(7)–Co(1)	117.0(9)	C(8′)–N(7′)–Co(2)	115.5(9)
C(8)–N(7)–O(3)	121.7(9)	C(8′)–N(7′)–O(3′)	122.2(10)
C(9)–C(8)–N(7)	122.5(11)	C(9′)–C(8′)–N(7′)	119.3(11)
C(10)–(C8)–N(7)	114.2(11)	C(10′)–C(8′)–N(7′)	114.2(12)
C(10)–C(8)–C(9)	123.0(11)	C(10′)–C(8′)–C(9′)	126.0(11)
C(11)–C(10)–C(8)	124.3(11)	C(11′)–C(10′)–C(8′)	125.2(11)
N(12)–C(10)–C(8)	112.4(11)	N(12′)–C(10′)–C(8′)	111.3(11)
N(12)–C(10)–C(11)	123.1(10)	N(12′)–C(10′)–C(11′)	123.2(10)
O(4)–N(12)–Co(1)	122.8(7)	O(4′)–N(12′)–Co(2)	123.0(7)
C(10)–N(12)–Co(1)	116.3(9)	C(10′)–N(12′)–Co(2)	117.5(8)
C(10)–N(12)–O(4)	120.9(9)	C(10′)–N(12′)–O(4′)	119.5(9)
C(14)–N(13)–Co(1)	120.9(7)	C(14′)–N(13′)–Co(2)	121.6(7)
C(18)–N(13)–Co(1)	120.1(7)	C(18′)–N(13′)–Co(2)	120.4(7)
C(18)–N(13)–C(14)	119.0(9)	C(18′)–N(13′)–C(14′)	117.9(9)
C(15)–C(14)–N(13)	120.9(10)	C(15′)–C(14′)–N(13′)	122.4(10)
C(16)–C(15)–C(14)	120.1(12)	C(16′)–C(15′)–C(14′)	117.5(11)
C(17)–C(16)–C(15)	119.1(12)	C(17′)–C(16′)–C(15′)	120.9(12)
C(18)–C(17)–C(16)	119.1(11)	C(18′)–C(17′)–C(16′)	117.1(13)
C(17)–C(18)–N(13)	121.7(11)	C(17′)–C(18′)–N(13′)	124.2(11)
Cl(1)–C(19)–Co(1)	114.9(7)	Cl(1′)–C(19′)–Co(2)	115.2(7)
C(20)–C(19)–Co(1)	134.7(10)	C(20′)–C(19′)–Co(2)	132.4(9)
C(20)–C(19)–Cl(1)	110.4(10)	C(20′)–C(19′)–Cl(1′)	111.0(9)
C(21)–C(20)–C(19)	128.1(11)	C(21′)–C(20′)–C(19′)	128.3(10)
C(27)–C(20)–C(19)	120.6(10)	C(27′)–C(20′)–C(19′)	121.9(10)
C(27)–C(20)–C(21)	111.3(10)	C(27′)–C(20′)–C(21′)	109.7(9)
C(22)–C(21)–C(20)	119.2(11)	C(22′)–C(21′)–C(20′)	115.0(11)
C(26)–C(21)–C(20)	120.2(10)	C(26′)–C(21′)–C(20′)	122.7(10)
C(26)–C(21)–C(22)	119.3(11)	C(26′)–C(21′)–C(22′)	121.7(11)
C(23)–C(22)–C(21)	122.8(12)	C(23′)–C(22′)–C(21′)	118.9(11)
C(24)–C(23)–C(22)	117.6(12)	C(24′)–C(23′)–C(22′)	118.2(11)
C(25)–C(24)–C(23)	120.0(13)	C(25′)–C(24′)–C(23′)	123.7(12)
C(23)–C(24)–Cl(2)	119.8(11)	C(23′)–C(24′)–Cl(2′)	118.7(10)
C(25)–C(24)–Cl(2)	120.2(11)	C(25′)–C(24′)–Cl(2′)	117.6(9)
C(26)–C(25)–C(24)	122.1(13)	C(26′)–C(25′)–C(24′)	118.9(11)
C(25)–C(26)–C(21)	118.0(12)	C(25′)–C(26′)–C(21′)	118.5(11)
C(31)–C(32)–C(27)	122.3(12)	C(31′)–C(32′)–C(27′)	118.8(11)

listed in Supplementary Publication No. SUP 21405 (22 pp., 1 microfiche).*

TABLE 5

Selected shortest non-bonded distances (Å)

Co(1) · · · O(1)	2.866	Co(2) · · · O(1′)	2.863
Co(1) · · · O(2)	2.823	Co(2) · · · O(2′)	2.864
Co(1) · · · O(3)	2.835	Co(2) · · · O(3′)	2.863
Co(1) · · · O(4)	2.842	Co(2) · · · O(4′)	2.827
O(2) · · · O(3)	2.505	O(2′) · · · O(3′)	2.503
O(1) · · · O(4)	2.499	O(1′) · · · O(4′)	2.498
Co(1) · · · Cl(1)	3.183	Co(2) · · · Cl(1′)	3.184
Cl(1) · · · C(10)	3.011	Cl(1′) · · · C(10′)	2.956
Cl(1) · · · N(12)	2.929	Cl(1′) · · · N(12′)	2.886
N(6) · · · C(18)	3.086	N(6′) · · · C(18′)	2.926
N(6) · · · C(19)	2.774	N(6′) · · · C(19′)	2.837
N(6) · · · C(20)	3.205	N(6′) · · · C(20′)	3.343
N(6) · · · C(21)	3.001	N(6′) · · · C(21′)	3.203
N(6) · · · C(22)	3.139	N(6′) · · · C(22′)	3.137

DISCUSSION

The asymmetric unit contains two molecules of very similar geometry, each with a chlorovinyl group σ-bonded to cobalt and two vicinal dioximes and a pyridine ligand completing the octahedral co-ordination. The oximes are held in the equatorial plane by O–H · · · O hydrogen bonds [mean O · · · O 2.50(1) Å].

The O · · · O distances are all very close to the critical value of 2.5 Å below which hydrogen bonds are said to become symmetrical.[8] Three of the four hydrogen-bonded hydrogen atoms refined freely to positions within 1σ of the geometric centres of these bonds, providing some evidence for a symmetrical disposition. However, an indication of the position of the hydrogen atoms may also be obtained from the relevant N–O distances which, if unequal, may indicate asymmetry with the hydrogen situated closest to the oxygen atom having the longer N–O distance.[9] In the present structure these distances are effectively equal for both the hydrogen-bonded bridges in molecule 2, but significantly different for the corresponding bridges in molecule 1, thus providing evidence for symmetrical hydrogen bonds in the former case only.

The O · · · O distances in both aquo- and pyridylmethylbis(dimethylglyoximato)cobalt(III) are <2.5 Å,[10,11] and the corresponding N–O distances are in each case very similar. In the former structure, however, the hydrogen-bonded hydrogen atoms refined to asymmetric positions.[10]

The pyridine molecules lie in similar positions to that found in other cobaloximes,[11] approximately in the plane, perpendicular to the oxime plane which contains the line separating the two oximes. The dimensions of the pyridinebis(dimethylglyoximato)cobalt(III) unit are similar to those in the analogous methyl and $CH_3O_2C \cdot CH_2$ derivatives.[11,12]

Although there are no significant differences in bond lengths between the two molecules of the title compound, it is apparent from Figures 1 and 2 that there are subtle differences in the relative orientations of the aromatic rings. This is probably related to the packing of this bulky compound in the crystal. Some degree of interaction between one aromatic ring and the equatorial ligands is also indicated, and the non-bonded distances involved (Table 5) are shortest in the case of N(6). The effect is apparent in the C(19′)–Co(2)–N(6′) bond angle of 95.0(5)° [mean for the corresponding angles in the two molecules is 91.8(10)]. That the latter value is somewhat higher than that [88.4(10)°] for the methyl derivative [11] is due to an overall repulsive effect of the bulky axial group. The bond angle corresponding to C(19)–Co–N(6) found in the $CH_3O_2 \cdot CH_2$ derivative is also large [94.9(3)°]; this is ascribed to a non-bonded interaction with the carboxy-carbon at 2.86 Å.[12]

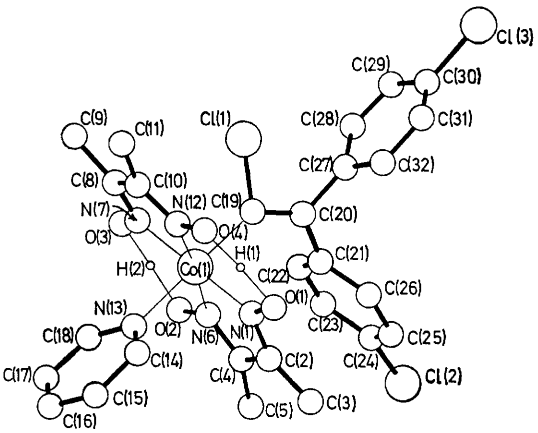

FIGURE 1 Molecule 1

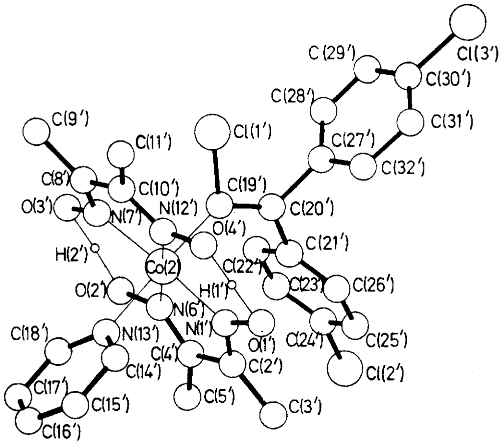

FIGURE 2 Molecule 2

Although several σ-bonded vinyl derivatives of cobalt(III) have been prepared from the reactions of cobalt(I) species with vinyl halides or acetylenes,[13,14]

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

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no such compound has previously been produced from a saturated organic molecule. The mean C=C distance [1.366(15) Å] compares with those for σ-vinyl complexes of bis(acetylacetone)ethylenedi-iminatocobalt(III) [1.333(15) Å],[15] and bis(salicylaldehyde)ethylenedi-iminatocobalt(III) [1.31(2) Å].[16] The corresponding single-bond distance in *p,p'*-DDT itself is 1.51(3) Å.[17] The deviation of the two phenyl rings from the ' butterfly ' [17] conformation is maintained in the present compound.

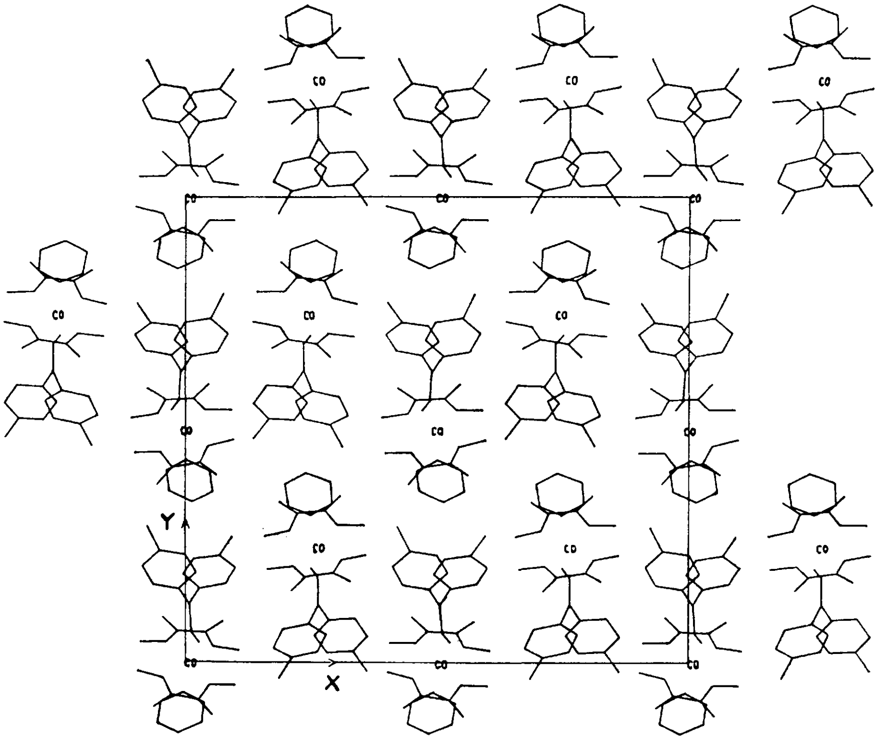

FIGURE 3 Projection of the structure perpendicular to Z; molecules 1 and 2 occur in alternate rows parallel to Y

DDT should be resistant to base-induced elimination of hydrogen chloride under the reaction conditions employed,[18,19] so it is likely that the hydrogen chloride elimination took place in the product of rapid S_N2 attack on C(2) of DDT. The vinylic double bond is stabilised by conjugation with the benzene rings, and the Co–C bond is stabilised by the vinylic chlorine.[20]

A σ-vinyl–cobalamin derivative provides a possible pathway for the extensive degradation of DDT sometimes observed in biological systems.[21] In the present case, precipitation from methanol solution probably prevented further reaction, since there is mass spectrometric and analytical evidence [22] for the rapid methanolysis of the vinylic chlorine in boiling methanol.

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