Synthesis, Structure, and the Unusual Reactivity of β-Halovinyl Cobalt Porphyrin Complexes - Supporting Information

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Table 1. Comparison of relevant bond lengths and angles from chlorovinyl cobalt complexes.

Chlorovinyl Co Complexes	Co-C (Å)	Co-C=C (deg)	C-Cl (Å)	C=C (Å)
Z-2-chlorovinyl B_{12}[a]	1.946(7)	140.1(9)	1.736(10)	1.291(7)
vinyl B_{12}[a]	1.911(7)	128.3(6)	-	1.286(8)
E-dichlorovinyl DMG[a]	1.945 (5)	121(2)	1-Cl 1.75(3) 2-Cl 1.758	1.32(3)
E-dichlorovinyl DMG[b]	1.958(3)	123.3(3)	1-Cl 1.740(3) 2-Cl 1.723(5)	1.324(7)
Z-2-chlorovinyl DMG[a]	1.946(2)	140.2(3)	*cis*-2-Cl 1.751(3)	1.314(3)
1-chlorovinyl DMG[a]	1.947(4)	126.7(3)	1-Cl 1.762(4)	1.341(4)
E-2-chlorovinyl DMG[b] (disordered)	1.931(1)	134.8(7) 132.1(6)	*trans*-2-Cl 1.795(16) 1.802(13)	1.192(13) 1.236(11)
vinyl DMG[a]	1.953(3)	127.8(3)	-	1.291(9)
Z -dichlorovinyl (TPP)[e]	1.929(4)	134.0(5)	1-Cl 1.757(7) 2-Cl 1.735(4)	1.320(7)

E -2-chlorovinyl (TPP)[d]	1.926(4)	126.7(3)	1.752(4)	1.234(5)
E -2-bromovinyl (TPP)[e]	1.925(4)	126.9(3)	1.927(4) Br	1.211(6)

[a]McCauley, et al.[1-3] [b]Jones, et al.[4] [c]Rich, et al.[5] [d]Fritsch, et al.[6] [e]This work.

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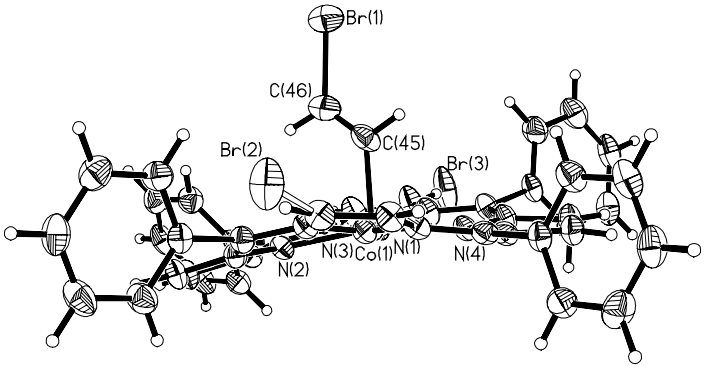
X-ray Report for 1

CRYSTAL STRUCTURE REPORT

$C_{46}\ H_{29.94}\ Br_{1.06}\ Co\ N_4$



Report prepared for:

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Data collection

A crystal (approximate dimensions 0.30 x 0.30 x 0.20 mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Siemens SMART Platform CCD diffractometer for a data collection at 173(2) K.[1] A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 131 reflections. The data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 15 seconds and a detector distance of 4.9 cm. A randomly oriented region of reciprocal space was surveyed to the extent of one sphere and to a resolution of 0.84 Å. Four major sections of frames were collected with 0.30º steps in ω at four different ϕ settings and a detector position of -28º in 2θ. The intensity data were corrected for absorption and decay (SADABS).[2] Final cell constants were calculated from the xyz centroids of 3812 strong reflections from the actual data collection after integration (SAINT).[3] Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

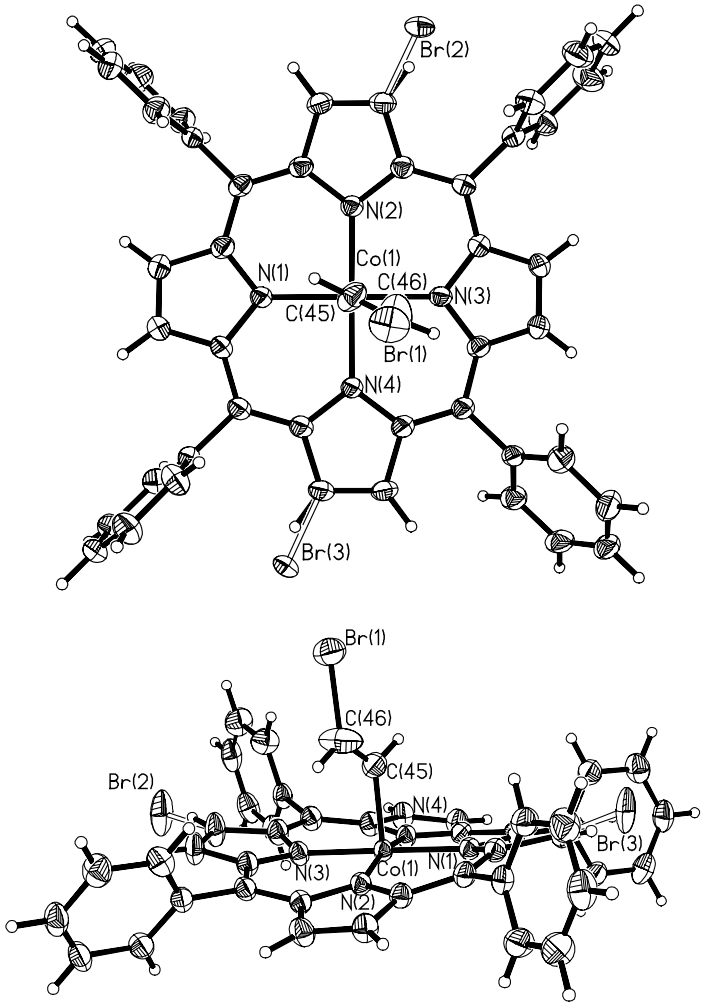
The structure was solved using SHELXS-97 (Sheldrick, 1990)[4] and refined using SHELXL-97 (Sheldrick, 1997).[4] The space group P-1 was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0447$ and $wR2 = 0.1242$ (F^2, all data).

Compositional disorder was observed in this structure with bromine atoms replacing a hydrogen approximately 3% of the time. This was observed at two positions on the porphyrin ring. ^{1}H NMR and ESI-TOF MS data suggest that a brominated porphyrin complex is present at less than 10%. This compositional impurity was modeled as disorder between the presence of a riding hydrogen atom and a bromine atom.

A solvent void of 147 $Å^3$ was found in the structure, and the Platon Squeeze program was used to removed the solvent diffraction intensity from the data set. Based on preliminary data refinements, methylene chloride is believed to reside in the void over two disordered confirmations.

Structure description

The structure is the one suggested.



Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, S146 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1)include Author's Name as a coauthor or 2)acknowledge Author's Name, Victor G. Young, Jr., and the X-Ray Crystallographic Laboratory.

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[1] SMART V5.054, Bruker Analytical X-ray Systems, Madison, WI (2001).

[2] An empirical correction for absorption anisotropy, R. Blessing, *Acta Cryst.* **A51**, 33-38 (1995).

[3] SAINT+ V6.45, Bruker Analytical X-Ray Systems, Madison, WI (2003).

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[5] A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna. Sir97: a new tool for crystal structure determination and refinement. *J. Appl. Cryst.* **32**, 115-

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Some equations of interest:

$$R_{int} = \Sigma |F_o^2 - < F_o^2 >| / \Sigma|F_o^2|$$

$$R_1 = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$$

$$wR2 = [\Sigma[w(F_o^2-F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}$$

$$\text{where } w = q / [\sigma^2 (F_o^2) + (a*P)^2 + b*P + d + e*\sin(\theta)]$$

$$\text{GooF} = S = [\Sigma[w(F_o^2-F_c^2)^2] / (n-p)]^{1/2}$$

Table 1. Crystal data and structure refinement for **1**.

Identification code	05204	
Empirical formula	C46 H29.94 Br1.06 Co N4	
Formula weight	777.58	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	*a* = 11.251(2) Å	α = 103.136(3)°
	b = 13.175(3) Å	β = 107.623(3)°
	c = 14.369(3) Å	γ = 102.179(3)°
Volume	1884.9(7) Å^3	
Z	2	
Density (calculated)	1.370 Mg/m^3	
Absorption coefficient	1.553 mm^{-1}	

F(000)	792
Crystal color, morphology	red-purple, block
Crystal size	0.30 x 0.30 x 0.20 mm^3
Theta range for data collection	1.57 to 25.11°
Index ranges	$-13 \le h \le 13$, $-15 \le k \le 15$, $-17 \le l \le 17$
Reflections collected	18247
Independent reflections	6642 [*R*(int) = 0.0284]
Observed reflections	5534
Completeness to theta = 25.11°	98.7%
Absorption correction	Multi-scan
Max. and min. transmission	0.73 and 0.6351
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6642 / 0 / 489
Goodness-of-fit on F^2	1.076
Final *R* indices [*I*>2sigma(*I*)]	*R*1 = 0.0447, *wR*2 = 0.1191
R indices (all data)	*R*1 = 0.0532, *wR*2 = 0.1242
Largest diff. peak and hole	0.982 and -0.899 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **1**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Co1	1750(1)	1279(1)	2031(1)	22(1)
Br1	677(1)	2368(1)	4908(1)	49(1)
N2	-73(3)	411(2)	1252(2)	24(1)
N1	2159(3)	-38(2)	2263(2)	24(1)
C2	3257(3)	-1162(3)	2935(3)	30(1)
N3	1338(3)	2587(2)	1781(2)	26(1)
C45	1632(4)	1714(3)	3364(3)	37(1)
C12	-641(3)	-692(3)	1084(2)	26(1)
C24	199(4)	3838(3)	1531(3)	40(1)
C1	3384(3)	-142(3)	2723(2)	26(1)
C17	-2294(3)	2105(2)	438(2)	27(1)
C4	1287(3)	-997(3)	2171(2)	26(1)
N4	3625(3)	2065(2)	2545(2)	26(1)

C6	-852(3)	-2454(3)	1476(3)	28(1)
C5	-51(3)	-1345(3)	1585(3)	27(1)
C15	-1091(3)	763(3)	751(2)	26(1)
C34	4204(3)	3174(3)	2767(3)	29(1)
C23	113(3)	2701(3)	1371(3)	29(1)
C26	2186(3)	3650(3)	2197(3)	31(1)
C46	670(5)	1808(4)	3545(3)	60(1)
C37	4670(3)	1656(3)	2837(2)	26(1)
C38	4570(3)	613(3)	2931(2)	26(1)
C28	4295(3)	5134(3)	3103(3)	30(1)
C16	-1040(3)	1852(3)	854(2)	26(1)
C39	5809(3)	318(2)	3300(3)	26(1)
C14	-2255(3)	-140(3)	190(3)	32(1)
C13	-1987(3)	-1034(3)	400(3)	31(1)
C29	4296(4)	5736(3)	4026(3)	40(1)
C42	8121(4)	-210(3)	3960(3)	41(1)
C40	6301(3)	-158(3)	2588(3)	35(1)
C44	6482(4)	521(3)	4337(3)	37(1)
C18	-3229(4)	1950(3)	881(3)	37(1)
C36	5894(3)	2504(3)	3184(3)	32(1)
C20	-4621(4)	2611(3)	-313(3)	40(1)
C22	-2532(3)	2523(3)	-384(3)	34(1)
C21	-3700(4)	2763(3)	-761(3)	39(1)
C35	5600(3)	3436(3)	3155(3)	34(1)
C19	-4381(4)	2207(3)	514(3)	42(1)
C7	-1034(4)	-2688(3)	2327(3)	34(1)
C9	-2325(4)	-4537(3)	1292(3)	43(1)
C11	-1417(4)	-3278(3)	530(3)	38(1)
C32	5675(4)	6756(3)	3027(3)	42(1)
C43	7636(4)	257(3)	4667(3)	41(1)
C33	4990(4)	5648(3)	2606(3)	38(1)
C31	5660(4)	7347(3)	3948(3)	44(1)
C8	-1772(4)	-3731(3)	2229(3)	41(1)
C41	7459(4)	-424(3)	2921(3)	44(1)
C10	-2157(4)	-4308(3)	440(3)	46(1)
C30	4975(4)	6849(3)	4447(3)	47(1)

C27	3530(3)	3942(3)	2664(3)	30(1)
C25	1476(4)	4417(3)	2036(3)	43(1)
Br2	1519(12)	-2892(9)	3011(12)	51(5)
C3	1969(3)	-1687(3)	2609(3)	30(1)
Br3	1841(13)	5844(10)	2263	
(15)	63(7)			

Table 3. Bond lengths [Å] and angles [°] for **1**.

Co(1)-C(45)	1.925(4)	C(17)-C(16)	1.495(4)
Co(1)-N(2)	1.951(3)	C(4)-C(5)	1.397(5)
Co(1)-N(3)	1.956(3)	C(4)-C(3)	1.440(4)
Co(1)-N(1)	1.960(3)	N(4)-C(37)	1.385(4)
Co(1)-N(4)	1.963(3)	N(4)-C(34)	1.386(4)
Br(1)-C(46)	1.927(4)	C(6)-C(7)	1.390(5)
N(2)-C(15)	1.386(4)	C(6)-C(11)	1.395(5)
N(2)-C(12)	1.392(4)	C(6)-C(5)	1.492(4)
N(1)-C(4)	1.378(4)	C(15)-C(16)	1.395(4)
N(1)-C(1)	1.387(4)	C(15)-C(14)	1.431(5)
C(2)-C(3)	1.347(5)	C(34)-C(27)	1.395(5)
C(2)-C(1)	1.432(4)	C(34)-C(35)	1.432(5)
C(2)-H(2A)	0.9500	C(23)-C(16)	1.383(5)
N(3)-C(23)	1.381(4)	C(26)-C(27)	1.381(5)
N(3)-C(26)	1.393(4)	C(26)-C(25)	1.431(5)
C(45)-C(46)	1.211(6)	C(46)-H(46A)	0.9500
C(45)-H(45A)	0.9500	C(37)-C(38)	1.395(5)
C(12)-C(5)	1.389(4)	C(37)-C(36)	1.441(5)
C(12)-C(13)	1.440(4)	C(38)-C(39)	1.501(4)
C(24)-C(25)	1.352(5)	C(28)-C(29)	1.382(5)
C(24)-C(23)	1.441(5)	C(28)-C(33)	1.384(5)
C(24)-H(24A)	0.9500	C(28)-C(27)	1.501(4)
C(1)-C(38)	1.387(5)	C(39)-C(44)	1.385(5)
C(17)-C(18)	1.388(5)	C(39)-C(40)	1.394(5)
C(17)-C(22)	1.392(5)	C(14)-C(13)	1.351(5)
		C(14)-H(14A)	0.9500
		C(13)-H(13A)	0.9500
		C(29)-C(30)	1.394(5)

C(29)-H(29A)	0.9500	C(10)-H(10A)	0.9500
C(42)-C(43)	1.379(6)	C(30)-H(30A)	0.9500
C(42)-C(41)	1.382(6)	C(25)-Br(3)	1.768(12)
C(42)-H(42A)	0.9500	C(25)-H(25A)	0.9500
C(40)-C(41)	1.394(5)	Br(2)-C(3)	1.835(12)
C(40)-H(40A)	0.9500	Br(2)-Br(3)#1	1.93(2)
C(44)-C(43)	1.387(5)	C(3)-H(3A)	0.9500
C(44)-H(44A)	0.9500	Br(3)-Br(2)#2	1.93(2)
C(18)-C(19)	1.388(5)		
C(18)-H(18A)	0.9500	C(45)-Co(1)-N(2)	98.00(14)
C(36)-C(35)	1.344(5)	C(45)-Co(1)-N(3)	89.70(14)
C(36)-H(36A)	0.9500	N(2)-Co(1)-N(3)	90.28(11)
C(20)-C(21)	1.379(6)	C(45)-Co(1)-N(1)	90.97(13)
C(20)-C(19)	1.387(6)	N(2)-Co(1)-N(1)	89.49(11)
C(20)-H(20A)	0.9500	N(3)-Co(1)-N(1)	179.31(11)
C(22)-C(21)	1.393(5)	C(45)-Co(1)-N(4)	93.59(14)
C(22)-H(22A)	0.9500	N(2)-Co(1)-N(4)	168.40(11)
C(21)-H(21A)	0.9500	N(3)-Co(1)-N(4)	89.96(11)
C(35)-H(35A)	0.9500	N(1)-Co(1)-N(4)	90.14(11)
C(19)-H(19A)	0.9500	C(15)-N(2)-C(12)	104.8(3)
C(7)-C(8)	1.398(5)	C(15)-N(2)-Co(1)	127.5(2)
C(7)-H(7A)	0.9500	C(12)-N(2)-Co(1)	127.7(2)
C(9)-C(8)	1.375(6)	C(4)-N(1)-C(1)	104.8(3)
C(9)-C(10)	1.382(6)	C(4)-N(1)-Co(1)	126.9(2)
C(9)-H(9A)	0.9500	C(1)-N(1)-Co(1)	127.4(2)
C(11)-C(10)	1.389(5)	C(3)-C(2)-C(1)	107.5(3)
C(11)-H(11A)	0.9500	C(3)-C(2)-H(2A)	126.2
C(32)-C(31)	1.381(6)	C(1)-C(2)-H(2A)	126.2
C(32)-C(33)	1.390(5)	C(23)-N(3)-C(26)	104.8(3)
C(32)-H(32A)	0.9500	C(23)-N(3)-Co(1)	127.3(2)
C(43)-H(43A)	0.9500	C(26)-N(3)-Co(1)	126.3(2)
C(33)-H(33A)	0.9500	C(46)-C(45)-Co(1)	126.9(3)
C(31)-C(30)	1.369(6)	C(46)-C(45)-H(45A)	116.6
C(31)-H(31A)	0.9500	Co(1)-C(45)-H(45A)	116.6
C(8)-H(8A)	0.9500	C(5)-C(12)-N(2)	125.4(3)
C(41)-H(41A)	0.9500	C(5)-C(12)-C(13)	124.3(3)

N(2)-C(12)-C(13)	109.9(3)	Br(1)-C(46)-H(46A)	118.0
C(25)-C(24)-C(23)	107.0(3)	N(4)-C(37)-C(38)	124.9(3)
C(25)-C(24)-H(24A)	126.5	N(4)-C(37)-C(36)	110.8(3)
C(23)-C(24)-H(24A)	126.5	C(38)-C(37)-C(36)	123.7(3)
N(1)-C(1)-C(38)	125.5(3)	C(1)-C(38)-C(37)	122.8(3)
N(1)-C(1)-C(2)	110.3(3)	C(1)-C(38)-C(39)	119.2(3)
C(38)-C(1)-C(2)	124.2(3)	C(37)-C(38)-C(39)	118.0(3)
C(18)-C(17)-C(22)	118.8(3)	C(29)-C(28)-C(33)	119.1(3)
C(18)-C(17)-C(16)	120.5(3)	C(29)-C(28)-C(27)	119.0(3)
C(22)-C(17)-C(16)	120.7(3)	C(33)-C(28)-C(27)	121.9(3)
N(1)-C(4)-C(5)	125.0(3)	C(23)-C(16)-C(15)	122.3(3)
N(1)-C(4)-C(3)	110.7(3)	C(23)-C(16)-C(17)	119.3(3)
C(5)-C(4)-C(3)	123.5(3)	C(15)-C(16)-C(17)	118.3(3)
C(37)-N(4)-C(34)	104.3(3)	C(44)-C(39)-C(40)	119.3(3)
C(37)-N(4)-Co(1)	128.0(2)	C(44)-C(39)-C(38)	121.1(3)
C(34)-N(4)-Co(1)	127.6(2)	C(40)-C(39)-C(38)	119.5(3)
C(7)-C(6)-C(11)	118.6(3)	C(13)-C(14)-C(15)	107.3(3)
C(7)-C(6)-C(5)	120.2(3)	C(13)-C(14)-H(14A)	126.4
C(11)-C(6)-C(5)	121.2(3)	C(15)-C(14)-H(14A)	126.4
C(12)-C(5)-C(4)	121.4(3)	C(14)-C(13)-C(12)	107.2(3)
C(12)-C(5)-C(6)	119.5(3)	C(14)-C(13)-H(13A)	126.4
C(4)-C(5)-C(6)	119.0(3)	C(12)-C(13)-H(13A)	126.4
N(2)-C(15)-C(16)	125.3(3)	C(28)-C(29)-C(30)	120.5(4)
N(2)-C(15)-C(14)	110.5(3)	C(28)-C(29)-H(29A)	119.7
C(16)-C(15)-C(14)	124.0(3)	C(30)-C(29)-H(29A)	119.7
N(4)-C(34)-C(27)	125.1(3)	C(43)-C(42)-C(41)	120.3(3)
N(4)-C(34)-C(35)	110.7(3)	C(43)-C(42)-H(42A)	119.8
C(27)-C(34)-C(35)	124.2(3)	C(41)-C(42)-H(42A)	119.8
N(3)-C(23)-C(16)	125.4(3)	C(39)-C(40)-C(41)	120.1(3)
N(3)-C(23)-C(24)	110.5(3)	C(39)-C(40)-H(40A)	120.0
C(16)-C(23)-C(24)	124.1(3)	C(41)-C(40)-H(40A)	120.0
C(27)-C(26)-N(3)	125.8(3)	C(39)-C(44)-C(43)	120.4(4)
C(27)-C(26)-C(25)	123.7(3)	C(39)-C(44)-H(44A)	119.8
N(3)-C(26)-C(25)	110.5(3)	C(43)-C(44)-H(44A)	119.8
C(45)-C(46)-Br(1)	123.9(4)	C(19)-C(18)-C(17)	120.8(4)
C(45)-C(46)-H(46A)	118.0	C(19)-C(18)-H(18A)	119.6

C(17)-C(18)-H(18A)	119.6	C(28)-C(33)-H(33A)	119.8
C(35)-C(36)-C(37)	106.7(3)	C(32)-C(33)-H(33A)	119.8
C(35)-C(36)-H(36A)	126.7	C(30)-C(31)-C(32)	120.4(3)
C(37)-C(36)-H(36A)	126.7	C(30)-C(31)-H(31A)	119.8
C(21)-C(20)-C(19)	119.4(3)	C(32)-C(31)-H(31A)	119.8
C(21)-C(20)-H(20A)	120.3	C(9)-C(8)-C(7)	120.6(4)
C(19)-C(20)-H(20A)	120.3	C(9)-C(8)-H(8A)	119.7
C(17)-C(22)-C(21)	120.2(4)	C(7)-C(8)-H(8A)	119.7
C(17)-C(22)-H(22A)	119.9	C(42)-C(41)-C(40)	119.8(4)
C(21)-C(22)-H(22A)	119.9	C(42)-C(41)-H(41A)	120.1
C(20)-C(21)-C(22)	120.6(4)	C(40)-C(41)-H(41A)	120.1
C(20)-C(21)-H(21A)	119.7	C(9)-C(10)-C(11)	120.4(4)
C(22)-C(21)-H(21A)	119.7	C(9)-C(10)-H(10A)	119.8
C(36)-C(35)-C(34)	107.5(3)	C(11)-C(10)-H(10A)	119.8
C(36)-C(35)-H(35A)	126.3	C(31)-C(30)-C(29)	119.8(4)
C(34)-C(35)-H(35A)	126.3	C(31)-C(30)-H(30A)	120.1
C(20)-C(19)-C(18)	120.2(4)	C(29)-C(30)-H(30A)	120.1
C(20)-C(19)-H(19A)	119.9	C(26)-C(27)-C(34)	122.6(3)
C(18)-C(19)-H(19A)	119.9	C(26)-C(27)-C(28)	118.8(3)
C(6)-C(7)-C(8)	120.2(3)	C(34)-C(27)-C(28)	118.6(3)
C(6)-C(7)-H(7A)	119.9	C(24)-C(25)-C(26)	107.2(3)
C(8)-C(7)-H(7A)	119.9	C(24)-C(25)-Br(3)	115.4(5)
C(8)-C(9)-C(10)	119.5(3)	C(26)-C(25)-Br(3)	137.3(5)
C(8)-C(9)-H(9A)	120.2	C(24)-C(25)-H(25A)	126.4
C(10)-C(9)-H(9A)	120.2	C(26)-C(25)-H(25A)	126.4
C(10)-C(11)-C(6)	120.6(4)	Br(3)-C(25)-H(25A)	11.2
C(10)-C(11)-H(11A)	119.7	C(3)-Br(2)-Br(3)#1	113.0(10)
C(6)-C(11)-H(11A)	119.7	C(2)-C(3)-C(4)	106.7(3)
C(31)-C(32)-C(33)	119.8(4)	C(2)-C(3)-Br(2)	116.6(4)
C(31)-C(32)-H(32A)	120.1	C(4)-C(3)-Br(2)	135.6(5)
C(33)-C(32)-H(32A)	120.1	C(2)-C(3)-H(3A)	126.7
C(42)-C(43)-C(44)	120.1(4)	C(4)-C(3)-H(3A)	126.7
C(42)-C(43)-H(43A)	120.0	Br(2)-C(3)-H(3A)	13.5
C(44)-C(43)-H(43A)	120.0	C(25)-Br(3)-Br(2)#2	140.8(12)
C(28)-C(33)-C(32)	120.4(4)		

Symmetry transformations used to generate equivalent atoms:

#1 x,y-1,z #2 x,y+1,z

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U_{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U_{12}\ ]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co1	22(1)	18(1)	23(1)	5(1)	4(1)	7(1)
Br1	63(1)	49(1)	42(1)	13(1)	26(1)	20(1)
N2	26(1)	19(1)	24(1)	6(1)	6(1)	8(1)
N1	25(1)	21(1)	24(1)	6(1)	7(1)	7(1)
C2	31(2)	28(2)	31(2)	12(1)	8(1)	14(1)
N3	24(1)	21(1)	28(1)	7(1)	2(1)	6(1)
C45	33(2)	40(2)	29(2)	2(2)	2(2)	17(2)
C12	24(2)	25(2)	28(2)	8(1)	9(1)	7(1)
C24	34(2)	24(2)	50(2)	7(2)	-1(2)	14(2)
C1	29(2)	23(2)	24(2)	5(1)	7(1)	11(1)
C17	25(2)	19(2)	27(2)	3(1)	1(1)	6(1)
C4	27(2)	24(2)	26(2)	7(1)	9(1)	9(1)
N4	25(1)	20(1)	27(1)	5(1)	5(1)	7(1)
C6	24(2)	24(2)	36(2)	10(1)	9(1)	10(1)
C5	28(2)	21(2)	30(2)	7(1)	10(1)	7(1)
C15	26(2)	26(2)	25(2)	8(1)	6(1)	10(1)
C34	27(2)	21(2)	32(2)	6(1)	5(1)	4(1)
C23	26(2)	26(2)	31(2)	8(1)	5(1)	9(1)
C26	30(2)	21(2)	34(2)	6(1)	3(1)	7(1)
C46	50(3)	88(4)	31(2)	7(2)	15(2)	9(2)
C37	27(2)	26(2)	25(2)	5(1)	8(1)	11(1)
C38	28(2)	27(2)	23(2)	4(1)	8(1)	14(1)
C28	23(2)	23(2)	35(2)	7(1)	1(1)	6(1)
C16	25(2)	26(2)	25(2)	9(1)	6(1)	9(1)
C39	23(2)	19(2)	34(2)	6(1)	7(1)	6(1)
C14	24(2)	29(2)	34(2)	10(1)	2(1)	5(1)
C13	25(2)	22(2)	36(2)	5(1)	3(1)	2(1)
C29	41(2)	30(2)	40(2)	6(2)	12(2)	1(2)

C42	29(2)	36(2)	58(3)	17(2)	10(2)	16(2)
C40	33(2)	33(2)	36(2)	6(2)	11(2)	14(2)
C44	35(2)	35(2)	35(2)	7(2)	6(2)	13(2)
C18	34(2)	39(2)	37(2)	14(2)	9(2)	11(2)
C36	24(2)	30(2)	38(2)	9(2)	8(2)	8(1)
C20	29(2)	33(2)	46(2)	6(2)	-2(2)	12(2)
C22	35(2)	32(2)	31(2)	10(2)	8(2)	12(2)
C21	38(2)	33(2)	35(2)	11(2)	-2(2)	15(2)
C35	27(2)	26(2)	43(2)	10(2)	8(2)	5(1)
C19	28(2)	47(2)	47(2)	13(2)	11(2)	12(2)
C7	40(2)	29(2)	35(2)	11(2)	15(2)	11(2)
C9	40(2)	26(2)	60(3)	19(2)	16(2)	5(2)
C11	45(2)	28(2)	35(2)	8(2)	12(2)	6(2)
C32	32(2)	34(2)	56(2)	24(2)	7(2)	6(2)
C43	32(2)	36(2)	44(2)	11(2)	0(2)	7(2)
C33	36(2)	34(2)	43(2)	15(2)	10(2)	10(2)
C31	33(2)	22(2)	62(3)	13(2)	-1(2)	4(2)
C8	47(2)	35(2)	48(2)	21(2)	23(2)	13(2)
C41	40(2)	39(2)	62(3)	13(2)	24(2)	20(2)
C10	54(2)	26(2)	43(2)	5(2)	7(2)	3(2)
C30	47(2)	31(2)	47(2)	2(2)	8(2)	5(2)
C27	30(2)	21(2)	32(2)	7(1)	5(1)	5(1)
C25	34(2)	20(2)	57(2)	7(2)	-3(2)	8(2)
Br2	41(7)	25(6)	90(11)	27(6)	18(6)	17(5)
C3	35(2)	25(2)	32(2)	12(1)	10(2)	12(1)
Br3	35(8)	16(7)	109(15)	11(7)	-2(7)	3(5)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **1**.

	x	y	z	U(eq)
H2A	3953	-1421	3249	36
H45A	2410	1872	3941	44
H24A	-508	4127	1321	48
H46A	-137	1593	2981	73
H14A	-3065	-115	-248	38
H13A	-2577	-1754	144	37
H29A	3831	5388	4378	48
H42A	8915	-386	4189	49
H40A	5846	-300	1874	42
H44A	6151	843	4826	44
H18A	-3078	1664	1442	44
H36A	6744	2420	3394	38
H20A	-5412	2783	-569	48
H22A	-1896	2646	-689	40
H21A	-3863	3033	-1332	46
H35A	6208	4140	3354	41
H19A	-5007	2106	830	50
H7A	-657	-2138	2978	41
H9A	-2819	-5245	1231	51
H11A	-1293	-3134	-58	45
H32A	6151	7105	2684	50
H43A	8092	398	5380	50
H33A	5000	5241	1972	46
H31A	6128	8104	4236	53
H8A	-1892	-3884	2815	49
H41A	7792	-752	2436	53
H10A	-2551	-4859	-211	55
H30A	4963	7260	5077	56
H25A	1835	5189	2246	51
H3A	1586	-2378	2657	36

Table 6. Torsion angles [°] for **1**.

C45-Co1-N2-C15	91.5(3)	Co1-N1-C1-C38	-13.0(5)
N3-Co1-N2-C15	1.8(3)	C4-N1-C1-C2	-1.4(3)
N1-Co1-N2-C15	-177.5(3)	Co1-N1-C1-C2	168.4(2)
N4-Co1-N2-C15	-89.4(6)	C3-C2-C1-N1	0.2(4)
C45-Co1-N2-C12	-87.8(3)	C3-C2-C1-C38	-178.5(3)
N3-Co1-N2-C12	-177.6(3)	C1-N1-C4-C5	-167.7(3)
N1-Co1-N2-C12	3.1(3)	Co1-N1-C4-C5	22.5(5)
N4-Co1-N2-C12	91.2(6)	C1-N1-C4-C3	2.0(3)
C45-Co1-N1-C4	79.3(3)	Co1-N1-C4-C3	-167.8(2)
N2-Co1-N1-C4	-18.7(3)	C45-Co1-N4-C37	95.5(3)
N3-Co1-N1-C4	-89(9)	N2-Co1-N4-C37	-83.6(6)
N4-Co1-N1-C4	172.9(3)	N3-Co1-N4-C37	-174.8(3)
C45-Co1-N1-C1	-88.3(3)	N1-Co1-N4-C37	4.5(3)
N2-Co1-N1-C1	173.7(3)	C45-Co1-N4-C34	-79.5(3)
N3-Co1-N1-C1	104(9)	N2-Co1-N4-C34	101.4(6)
N4-Co1-N1-C1	5.3(3)	N3-Co1-N4-C34	10.2(3)
C45-Co1-N3-C23	-87.6(3)	N1-Co1-N4-C34	-170.5(3)
N2-Co1-N3-C23	10.4(3)	N2-C12-C5-C4	-12.9(5)
N1-Co1-N3-C23	80(9)	C13-C12-C5-C4	174.6(3)
N4-Co1-N3-C23	178.8(3)	N2-C12-C5-C6	168.6(3)
C45-Co1-N3-C26	76.1(3)	C13-C12-C5-C6	-3.9(5)
N2-Co1-N3-C26	174.1(3)	N1-C4-C5-C12	-4.4(5)
N1-Co1-N3-C26	-116(9)	C3-C4-C5-C12	-172.9(3)
N4-Co1-N3-C26	-17.5(3)	N1-C4-C5-C6	174.1(3)
N2-Co1-C45-C46	-26.8(5)	C3-C4-C5-C6	5.6(5)
N3-Co1-C45-C46	63.4(5)	C7-C6-C5-C12	-115.5(4)
N1-Co1-C45-C46	-116.4(5)	C11-C6-C5-C12	65.5(4)
N4-Co1-C45-C46	153.4(5)	C7-C6-C5-C4	66.0(4)
C15-N2-C12-C5	-168.3(3)	C11-C6-C5-C4	-113.1(4)
Co1-N2-C12-C5	11.2(5)	C12-N2-C15-C16	168.3(3)
C15-N2-C12-C13	5.1(4)	Co1-N2-C15-C16	-11.2(5)
Co1-N2-C12-C13	-175.4(2)	C12-N2-C15-C14	-5.7(4)
C4-N1-C1-C38	177.2(3)	Co1-N2-C15-C14	174.8(2)

C37-N4-C34-C27	-175.6(3)	C22-C17-C16-C23	69.1(4)
Co1-N4-C34-C27	0.4(5)	C18-C17-C16-C15	67.2(4)
C37-N4-C34-C35	2.4(4)	C22-C17-C16-C15	-114.3(4)
Co1-N4-C34-C35	178.3(2)	C1-C38-C39-C44	-89.1(4)
C26-N3-C23-C16	178.5(3)	C37-C38-C39-C44	89.3(4)
Co1-N3-C23-C16	-15.1(5)	C1-C38-C39-C40	91.6(4)
C26-N3-C23-C24	0.1(4)	C37-C38-C39-C40	-90.0(4)
Co1-N3-C23-C24	166.5(3)	N2-C15-C14-C13	4.2(4)
C25-C24-C23-N3	0.1(5)	C16-C15-C14-C13	-169.8(3)
C25-C24-C23-C16	-178.3(4)	C15-C14-C13-C12	-0.9(4)
C23-N3-C26-C27	-177.7(4)	C5-C12-C13-C14	170.8(3)
Co1-N3-C26-C27	15.7(5)	N2-C12-C13-C14	-2.7(4)
C23-N3-C26-C25	-0.2(4)	C33-C28-C29-C30	0.8(5)
Co1-N3-C26-C25	-166.8(3)	C27-C28-C29-C30	-178.8(3)
Co1-C45-C46-Br1	-174.5(2)	C44-C39-C40-C41	0.0(5)
C34-N4-C37-C38	167.9(3)	C38-C39-C40-C41	179.3(3)
Co1-N4-C37-C38	-8.1(5)	C40-C39-C44-C43	0.2(5)
C34-N4-C37-C36	-3.3(4)	C38-C39-C44-C43	-179.1(3)
Co1-N4-C37-C36	-179.2(2)	C22-C17-C18-C19	-0.1(5)
N1-C1-C38-C37	10.0(5)	C16-C17-C18-C19	178.5(3)
C2-C1-C38-C37	-171.6(3)	N4-C37-C36-C35	3.1(4)
N1-C1-C38-C39	-171.7(3)	C38-C37-C36-C35	-168.2(3)
C2-C1-C38-C39	6.7(5)	C18-C17-C22-C21	-1.0(5)
N4-C37-C38-C1	0.9(5)	C16-C17-C22-C21	-179.6(3)
C36-C37-C38-C1	170.9(3)	C19-C20-C21-C22	-0.6(5)
N4-C37-C38-C39	-177.5(3)	C17-C22-C21-C20	1.4(5)
C36-C37-C38-C39	-7.4(5)	C37-C36-C35-C34	-1.5(4)
N3-C23-C16-C15	4.4(5)	N4-C34-C35-C36	-0.6(4)
C24-C23-C16-C15	-177.4(3)	C27-C34-C35-C36	177.4(3)
N3-C23-C16-C17	-179.1(3)	C21-C20-C19-C18	-0.5(6)
C24-C23-C16-C17	-0.9(5)	C17-C18-C19-C20	0.8(6)
N2-C15-C16-C23	9.2(5)	C11-C6-C7-C8	-0.1(5)
C14-C15-C16-C23	-177.7(3)	C5-C6-C7-C8	-179.2(3)
N2-C15-C16-C17	-167.4(3)	C7-C6-C11-C10	0.7(5)
C14-C15-C16-C17	5.8(5)	C5-C6-C11-C10	179.8(3)
C18-C17-C16-C23	-109.4(4)	C41-C42-C43-C44	-0.4(6)

C39-C44-C43-C42	0.0(6)	C5-C4-C3-Br2	-25.6(9)
C29-C28-C33-C32	-0.3(5)	Br3#1-Br2-C3-C2	-75.2(9)
C27-C28-C33-C32	179.2(3)	Br3#1-Br2-C3-C4	119.2(7)
C31-C32-C33-C28	0.0(5)	C24-C25-Br3-Br2#2	64.7(17)
C33-C32-C31-C30	0.0(6)	C26-C25-Br3-Br2#2	-119.4(13)
C10-C9-C8-C7	-0.5(6)		
C6-C7-C8-C9	0.0(6)		
C43-C42-C41-C40	0.5(6)		
C39-C40-C41-C42	-0.4(6)		
C8-C9-C10-C11	1.1(6)		
C6-C11-C10-C9	-1.2(6)		
C32-C31-C30-C29	0.5(6)		
C28-C29-C30-C31	-0.8(6)		
N3-C26-C27-C34	0.3(6)		
C25-C26-C27-C34	-176.8(4)		
N3-C26-C27-C28	-178.0(3)		
C25-C26-C27-C28	4.8(6)		
N4-C34-C27-C26	-8.6(6)		
C35-C34-C27-C26	173.7(4)		
N4-C34-C27-C28	169.7(3)		
C35-C34-C27-C28	-8.0(5)		
C29-C28-C27-C26	76.3(4)		
C33-C28-C27-C26	-103.2(4)		
C29-C28-C27-C34	-102.1(4)		
C33-C28-C27-C34	78.4(4)		
C23-C24-C25-C26	-0.3(5)		
C23-C24-C25-Br3	176.8(8)		
C27-C26-C25-C24	177.9(4)		
N3-C26-C25-C24	0.3(5)		
C27-C26-C25-Br3	1.8(12)		
N3-C26-C25-Br3	-175.8(11)		
C1-C2-C3-C4	1.0(4)		
C1-C2-C3-Br2	-168.4(6)		
N1-C4-C3-C2	-2.0(4)		
C5-C4-C3-C2	167.9(3)		
N1-C4-C3-Br2	164.5(7)		

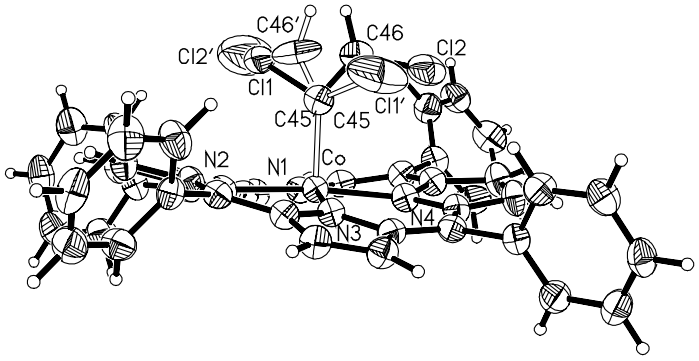
Symmetry transformations used to generate equivalent atoms:

#1 x,y-1,z #2 x,y+1,z

X-ray Report for 3

CRYSTAL STRUCTURE REPORT

$C_{46}\ H_{29}\ C_{l2}\ Co\ N_4$



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Data collection

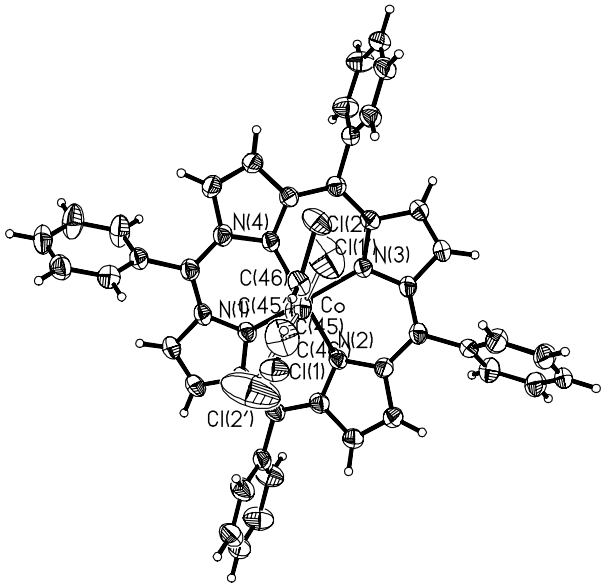
A crystal (approximate dimensions 0.40 x 0.40 x 0.20 mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Siemens SMART PLatform CCD diffractometer for a data collection at 173(2) K.[1] A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 3754 reflections. The data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 10 seconds and a detector distance of **??** cm. A randomly oriented region of reciprocal space was surveyed to the extent of one sphere and to a resolution of 0.84 Å. Four major sections of frames were collected with 0.30º steps in ω at four different ϕ settings and a detector position of -28º in 2θ. The intensity data were corrected for absorption and decay (SADABS).[2] Final cell constants were calculated from the xyz centroids of 3754 strong reflections from the actual data collection after integration (SAINT).[3] Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SIR-97 [5] and refined using SHELXL-97 (Sheldrick, 1997).[4] The space group P-1 was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to R_1 = 0.0391 and wR_2 = 0.1052 (F^2, all data).

Structure description

The structure is the one suggested.



The structure refinement included the treatment for disorder in the dichlorovinyl group. Between the two position, an occupancy of 77:23 was observed. For the major component, the thermal parameters for dichlorovinyl group were fine, but in the minor component the thermal parameters are a bit larger. The thermal parameters for C45' were set to the same values for C45 (EADP), but this approach was not appropriate for C46', Cl1' or Cl2' since the nearest atoms on the major component were greater than 1 Angstrom away. As a result, the thermal ellipsoids are larger for the minor component.

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, S146 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1)include Author's Name as a coauthor or 2)acknowledge Author's Name, Victor G. Young, Jr., and the X-Ray Crystallographic Laboratory.

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[1] SMART V5.054, Bruker Analytical X-ray Systems, Madison, WI (2001).

[2] An empirical correction for absorption anisotropy, R. Blessing, *Acta Cryst.* **A51**, 33-38 (1995).

[3] SAINT+ V6.45, Bruker Analytical X-Ray Systems, Madison, WI (2003).

[4] SHELXTL V6.14, Bruker Analytical X-Ray Systems, Madison, WI (2000).

[5] A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna. Sir97: a new tool for crystal structure determination and refinement. *J. Appl. Cryst.* **32**, 115-119 (1998).

[6] M. C. Burla, M. Camalli, B. Carrozzini, G. L. Cascarano, C. Giacovazzo, G. Polidori, R. Spagna. Sir2002: a new Direct Methods program for automatic solution and refinement of crystal structures. *J. Appl. Cryst.* (2003), in preparation.

[7] A. L. Spek, *Acta. Cryst.* **A46**, C34 (1990). PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, A. L. Spek (2000).

Some equations of interest:

$$R_{int} = \Sigma\, |F_o^2 - < F_o^2 >| \,/\, \Sigma |F_o^2|$$

$$R_1 = \Sigma ||F_o| - |F_c|| \,/\, \Sigma |F_o|$$

$$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] \,/\, \Sigma\,[w(F_o^2)^2]]^{1/2}$$

$$\text{where } w = q \,/\, [\sigma^2 (F_o^2) + (a*P)^2 + b*P + d + e*\sin(\theta)]$$

$$\text{GooF} = S = [\Sigma[w(F_o^2 - F_c^2)^2] \,/\, (n-p)]^{1/2}$$

Table 1. Crystal data and structure refinement for **3**.

Identification code	05026

Empirical formula	$C_{46}\ H_{29}\ Cl_2\ Co\ N_4$	
Formula weight	767.56	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.2370(15) Å	α = 67.209(2)°
	b = 12.3804(15) Å	β = 86.051(2)°
	c = 13.7944(17) Å	γ = 66.063(2)°
Volume	1751.3(4) $Å^3$	
Z	2	
Density (calculated)	1.456 Mg/m^3	
Absorption coefficient	0.684 mm^{-1}	
F(000)	788	
Crystal color, morphology	purple, plate	
Crystal size	0.40 x 0.40 x 0.20 mm^3	
Theta range for data collection	1.61 to 25.07°	
Index ranges	$-14 \le h \le 14$, $-14 \le k \le 14$, $-16 \le l \le 16$	
Reflections collected	17146	
Independent reflections	6184 [R(int) = 0.0232]	
Observed reflections	5339	
Completeness to theta = 25.07°	99.4%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.8753 and 0.7714	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6184 / 16 / 509	
Goodness-of-fit on F^2	1.064	
Final R indices [I>2sigma(I)]	R1 = 0.0391, wR2 = 0.1006	
R indices (all data)	R1 = 0.0473, wR2 = 0.1052	
Largest diff. peak and hole	0.426 and -0.284 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **3**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}

Co	9269(1)	485(1)	2898(1)	29(1)
N1	10029(2)	1280(2)	1710(2)	33(1)
N2	10735(2)	-1104(2)	3361(2)	31(1)
N3	8697(2)	-151(2)	4273(2)	32(1)
N4	7874(2)	2135(2)	2507(2)	33(1)
C1	9492(2)	2458(2)	878(2)	35(1)
C2	10359(2)	2707(3)	168(2)	42(1)
C3	11402(2)	1669(3)	544(2)	41(1)
C4	11203(2)	753(2)	1481(2)	35(1)
C5	12006(2)	-506(2)	1979(2)	36(1)
C6	13183(2)	-977(3)	1537(2)	39(1)
C7	13250(3)	-1385(3)	726(2)	53(1)
C8	14342(3)	-1846(3)	324(2)	62(1)
C9	15357(3)	-1874(3)	735(3)	57(1)
C10	15295(3)	-1474(3)	1535(3)	64(1)
C11	14218(3)	-1024(3)	1942(3)	56(1)
C12	11735(2)	-1397(2)	2820(2)	35(1)
C13	12453(2)	-2752(3)	3247(2)	42(1)
C14	11910(2)	-3297(2)	4056(2)	39(1)
C15	10865(2)	-2266(2)	4150(2)	33(1)
C16	10167(2)	-2410(2)	4988(2)	32(1)
C17	10536(2)	-3707(2)	5876(2)	33(1)
C18	11574(3)	-4218(3)	6555(2)	44(1)
C19	11936(3)	-5419(3)	7370(2)	49(1)
C20	11270(3)	-6131(3)	7514(2)	47(1)
C21	10251(3)	-5647(3)	6853(3)	53(1)
C22	9875(2)	-4434(3)	6037(2)	47(1)
C23	9200(2)	-1375(2)	5066(2)	32(1)
C24	8570(2)	-1424(2)	5989(2)	37(1)
C25	7661(2)	-265(2)	5751(2)	37(1)
C26	7706(2)	525(2)	4677(2)	32(1)
C27	6829(2)	1736(2)	4113(2)	33(1)
C28	5698(2)	2215(2)	4605(2)	33(1)
C29	4868(2)	1690(3)	4702(2)	40(1)
C30	3816(2)	2110(3)	5154(2)	44(1)

C31	3587(2)	3048(3)	5530(2)	44(1)
C32	4398(3)	3577(3)	5445(3)	53(1)
C33	5445(2)	3174(3)	4972(2)	46(1)
C34	6897(2)	2462(2)	3070(2)	34(1)
C35	5950(2)	3650(3)	2422(2)	42(1)
C36	6328(2)	4054(3)	1461(2)	43(1)
C37	7534(2)	3139(2)	1517(2)	36(1)
C38	8292(2)	3304(2)	728(2)	37(1)
C39	7838(2)	4451(2)	-299(2)	39(1)
C40	7553(3)	5676(3)	-356(2)	62(1)
C41	7151(4)	6729(3)	-1314(3)	70(1)
C42	7050(3)	6566(3)	-2224(2)	55(1)
C43	7318(3)	5357(3)	-2178(2)	50(1)
C44	7707(3)	4305(3)	-1225(2)	47(1)
Cl1	9571(1)	-839(1)	1319(1)	49(1)
C45	8597(8)	-128(11)	2106(5)	35(1)
C46	7541(3)	-157(3)	2026(3)	40(1)
Cl2	6292(1)	452(1)	2642(1)	53(1)
Cl1'	7150(9)	-170(10)	2716(6)	105(3)
C45'	8550(40)	-240(60)	2290(30)	35(1)
C46'	8744(19)	-590(20)	1518(15)	77(6)
Cl2'	9978(8)	-684(13)	779(10)	155(5)

Table 3. Bond lengths [Å] and angles [°] for **3**.

Co-C(45')	1.898(15)	N(2)-C(12)	1.381(3)
Co-C(45)	1.929(4)	N(3)-C(23)	1.386(3)
Co-N(1)	1.9498(19)	N(3)-C(26)	1.388(3)
Co-N(3)	1.9527(19)	N(4)-C(34)	1.386(3)
Co-N(2)	1.954(2)	N(4)-C(37)	1.388(3)
Co-N(4)	1.955(2)	C(1)-C(38)	1.387(4)
N(1)-C(1)	1.380(3)	C(1)-C(2)	1.438(3)
N(1)-C(4)	1.388(3)	C(2)-C(3)	1.339(4)
N(2)-C(15)	1.380(3)	C(2)-H(2A)	0.9500
		C(3)-C(4)	1.436(3)
		C(3)-H(3A)	0.9500

C(4)-C(5)	1.374(4)	C(24)-C(25)	1.339(4)
C(5)-C(12)	1.388(3)	C(24)-H(24A)	0.9500
C(5)-C(6)	1.502(3)	C(25)-C(26)	1.436(3)
C(6)-C(7)	1.380(4)	C(25)-H(25A)	0.9500
C(6)-C(11)	1.390(4)	C(26)-C(27)	1.383(3)
C(7)-C(8)	1.394(4)	C(27)-C(34)	1.389(3)
C(7)-H(7A)	0.9500	C(27)-C(28)	1.498(3)
C(8)-C(9)	1.382(5)	C(28)-C(33)	1.382(4)
C(8)-H(8A)	0.9500	C(28)-C(29)	1.386(4)
C(9)-C(10)	1.361(5)	C(29)-C(30)	1.383(4)
C(9)-H(9A)	0.9500	C(29)-H(29A)	0.9500
C(10)-C(11)	1.381(4)	C(30)-C(31)	1.371(4)
		C(30)-H(30A)	0.9500
		C(31)-C(32)	1.371(4)
C(10)-H(10A)	0.9500	C(31)-H(31A)	0.9500
C(11)-H(11A)	0.9500	C(32)-C(33)	1.391(4)
C(12)-C(13)	1.430(4)	C(32)-H(32A)	0.9500
C(13)-C(14)	1.350(4)	C(33)-H(33A)	0.9500
C(13)-H(13A)	0.9500	C(34)-C(35)	1.430(3)
C(14)-C(15)	1.435(3)	C(35)-C(36)	1.346(4)
C(14)-H(14A)	0.9500	C(35)-H(35A)	0.9500
C(15)-C(16)	1.388(3)	C(36)-C(37)	1.436(4)
C(16)-C(23)	1.383(3)	C(36)-H(36A)	0.9500
C(16)-C(17)	1.499(3)	C(37)-C(38)	1.388(4)
C(17)-C(22)	1.389(4)	C(38)-C(39)	1.497(3)
C(17)-C(18)	1.394(4)	C(39)-C(40)	1.381(4)
C(18)-C(19)	1.382(4)	C(39)-C(44)	1.386(4)
C(18)-H(18A)	0.9500	C(40)-C(41)	1.387(4)
C(19)-C(20)	1.381(4)	C(40)-H(40A)	0.9500
C(19)-H(19A)	0.9500	C(41)-C(42)	1.368(5)
C(20)-C(21)	1.368(4)	C(41)-H(41A)	0.9500
C(20)-H(20A)	0.9500	C(42)-C(43)	1.373(4)
C(21)-C(22)	1.391(4)	C(42)-H(42A)	0.9500
C(21)-H(21A)	0.9500	C(43)-C(44)	1.380(4)
C(22)-H(22A)	0.9500	C(43)-H(43A)	0.9500
C(23)-C(24)	1.436(3)	C(44)-H(44A)	0.9500

Cl(1)-C(45)	1.757(7)	C(37)-N(4)-Co	126.55(17)
C(45)-C(46)	1.320(7)	N(1)-C(1)-C(38)	126.0(2)
C(46)-Cl(2)	1.735(4)	N(1)-C(1)-C(2)	110.4(2)
C(46)-H(46A)	0.9500	C(38)-C(1)-C(2)	123.6(2)
Cl(1')-C(45')	1.75(2)	C(3)-C(2)-C(1)	106.8(2)
C(45')-C(46')	1.278(17)	C(3)-C(2)-H(2A)	126.6
C(46')-Cl(2')	1.753(16)	C(1)-C(2)-H(2A)	126.6
C(46')-H(46B)	0.9500	C(2)-C(3)-C(4)	107.9(2)
Cl(2')-Cl(2')#1	2.17(3)	C(2)-C(3)-H(3A)	126.1
		C(4)-C(3)-H(3A)	126.1
C(45')-Co-C(45)	7.5(13)	C(5)-C(4)-N(1)	125.5(2)
C(45')-Co-N(1)	101.2(10)	C(5)-C(4)-C(3)	124.3(2)
C(45)-Co-N(1)	93.75(18)	N(1)-C(4)-C(3)	109.6(2)
C(45')-Co-N(3)	93.2(10)	C(4)-C(5)-C(12)	122.7(2)
C(45)-Co-N(3)	100.69(18)	C(4)-C(5)-C(6)	119.1(2)
N(1)-Co-N(3)	165.56(8)	C(12)-C(5)-C(6)	118.0(2)
C(45')-Co-N(2)	90.5(17)	C(7)-C(6)-C(11)	119.0(3)
C(45)-Co-N(2)	91.5(4)	C(7)-C(6)-C(5)	120.0(2)
N(1)-Co-N(2)	90.14(8)	C(11)-C(6)-C(5)	121.0(3)
N(3)-Co-N(2)	89.21(8)	C(6)-C(7)-C(8)	120.5(3)
C(45')-Co-N(4)	95.0(17)	C(6)-C(7)-H(7A)	119.8
C(45)-Co-N(4)	93.9(4)	C(8)-C(7)-H(7A)	119.8
N(1)-Co-N(4)	89.22(8)	C(9)-C(8)-C(7)	119.4(3)
N(3)-Co-N(4)	90.05(8)	C(9)-C(8)-H(8A)	120.3
N(2)-Co-N(4)	174.51(8)	C(7)-C(8)-H(8A)	120.3
C(1)-N(1)-C(4)	105.02(19)	C(10)-C(9)-C(8)	120.3(3)
C(1)-N(1)-Co	127.31(16)	C(10)-C(9)-H(9A)	119.8
C(4)-N(1)-Co	127.56(16)	C(8)-C(9)-H(9A)	119.8
C(15)-N(2)-C(12)	104.78(19)	C(9)-C(10)-C(11)	120.6(3)
C(15)-N(2)-Co	126.19(15)	C(9)-C(10)-H(10A)	119.7
C(12)-N(2)-Co	127.22(16)	C(11)-C(10)-H(10A)	119.7
C(23)-N(3)-C(26)	104.72(19)	C(10)-C(11)-C(6)	120.2(3)
C(23)-N(3)-Co	127.59(16)	C(10)-C(11)-H(11A)	119.9
C(26)-N(3)-Co	127.68(16)	C(6)-C(11)-H(11A)	119.9
C(34)-N(4)-C(37)	104.5(2)	N(2)-C(12)-C(5)	125.0(2)
C(34)-N(4)-Co	127.85(16)	N(2)-C(12)-C(13)	110.4(2)

C(5)-C(12)-C(13)	124.6(2)	C(23)-C(24)-H(24A)	126.4
C(14)-C(13)-C(12)	107.4(2)	C(24)-C(25)-C(26)	107.7(2)
C(14)-C(13)-H(13A)	126.3	C(24)-C(25)-H(25A)	126.2
C(12)-C(13)-H(13A)	126.3	C(26)-C(25)-H(25A)	126.2
C(13)-C(14)-C(15)	106.6(2)	C(27)-C(26)-N(3)	125.5(2)
C(13)-C(14)-H(14A)	126.7	C(27)-C(26)-C(25)	124.3(2)
C(15)-C(14)-H(14A)	126.7	N(3)-C(26)-C(25)	109.9(2)
N(2)-C(15)-C(16)	124.8(2)	C(26)-C(27)-C(34)	122.5(2)
N(2)-C(15)-C(14)	110.7(2)	C(26)-C(27)-C(28)	118.5(2)
C(16)-C(15)-C(14)	124.1(2)	C(34)-C(27)-C(28)	118.6(2)
C(23)-C(16)-C(15)	121.9(2)	C(33)-C(28)-C(29)	118.1(2)
C(23)-C(16)-C(17)	119.2(2)	C(33)-C(28)-C(27)	122.1(2)
C(15)-C(16)-C(17)	118.7(2)	C(29)-C(28)-C(27)	119.8(2)
C(22)-C(17)-C(18)	118.4(2)	C(30)-C(29)-C(28)	121.2(3)
C(22)-C(17)-C(16)	121.5(2)	C(30)-C(29)-H(29A)	119.4
C(18)-C(17)-C(16)	120.1(2)	C(28)-C(29)-H(29A)	119.4
C(19)-C(18)-C(17)	120.9(3)	C(31)-C(30)-C(29)	120.0(3)
C(19)-C(18)-H(18A)	119.6	C(31)-C(30)-H(30A)	120.0
C(17)-C(18)-H(18A)	119.6	C(29)-C(30)-H(30A)	120.0
C(20)-C(19)-C(18)	119.9(3)	C(30)-C(31)-C(32)	119.7(3)
C(20)-C(19)-H(19A)	120.0	C(30)-C(31)-H(31A)	120.1
C(18)-C(19)-H(19A)	120.0	C(32)-C(31)-H(31A)	120.1
C(21)-C(20)-C(19)	120.1(3)	C(31)-C(32)-C(33)	120.3(3)
C(21)-C(20)-H(20A)	120.0	C(31)-C(32)-H(32A)	119.8
C(19)-C(20)-H(20A)	120.0	C(33)-C(32)-H(32A)	119.8
C(20)-C(21)-C(22)	120.4(3)	C(28)-C(33)-C(32)	120.6(3)
C(20)-C(21)-H(21A)	119.8	C(28)-C(33)-H(33A)	119.7
C(22)-C(21)-H(21A)	119.8	C(32)-C(33)-H(33A)	119.7
C(17)-C(22)-C(21)	120.4(3)	N(4)-C(34)-C(27)	125.1(2)
C(17)-C(22)-H(22A)	119.8	N(4)-C(34)-C(35)	110.6(2)
C(21)-C(22)-H(22A)	119.8	C(27)-C(34)-C(35)	124.3(2)
C(16)-C(23)-N(3)	125.3(2)	C(36)-C(35)-C(34)	107.4(2)
C(16)-C(23)-C(24)	124.3(2)	C(36)-C(35)-H(35A)	126.3
N(3)-C(23)-C(24)	110.4(2)	C(34)-C(35)-H(35A)	126.3
C(25)-C(24)-C(23)	107.1(2)	C(35)-C(36)-C(37)	107.0(2)
C(25)-C(24)-H(24A)	126.4	C(35)-C(36)-H(36A)	126.5

C(37)-C(36)-H(36A)	126.5	C(42)-C(43)-C(44)	120.6(3)
N(4)-C(37)-C(38)	124.8(2)	C(42)-C(43)-H(43A)	119.7
N(4)-C(37)-C(36)	110.5(2)	C(44)-C(43)-H(43A)	119.7
C(38)-C(37)-C(36)	124.4(2)	C(43)-C(44)-C(39)	120.6(3)
C(1)-C(38)-C(37)	121.7(2)	C(43)-C(44)-H(44A)	119.7
C(1)-C(38)-C(39)	118.1(2)	C(39)-C(44)-H(44A)	119.7
C(37)-C(38)-C(39)	120.2(2)	C(46)-C(45)-Cl(1)	110.3(3)
C(40)-C(39)-C(44)	118.2(2)	C(46)-C(45)-Co	134.0(5)
C(40)-C(39)-C(38)	121.4(2)	Cl(1)-C(45)-Co	115.6(4)
C(44)-C(39)-C(38)	120.4(2)	C(45)-C(46)-Cl(2)	126.9(4)
C(39)-C(40)-C(41)	120.9(3)	C(45)-C(46)-H(46A)	116.6
C(39)-C(40)-H(40A)	119.5	Cl(2)-C(46)-H(46A)	116.6
C(41)-C(40)-H(40A)	119.5	C(46')-C(45')-Cl(1')	109.8(14)
C(42)-C(41)-C(40)	120.2(3)	C(46')-C(45')-Co	134.9(16)
C(42)-C(41)-H(41A)	119.9	Cl(1')-C(45')-Co	114.3(12)
C(40)-C(41)-H(41A)	119.9	C(45')-C(46')-Cl(2')	125.7(15)
C(41)-C(42)-C(43)	119.5(3)	C(45')-C(46')-H(46B)	117.1
C(41)-C(42)-H(42A)	120.3	Cl(2')-C(46')-H(46B)	117.1
C(43)-C(42)-H(42A)	120.3	C(46')-Cl(2')-Cl(2')#1	127.4(11)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y,-z

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U_{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U_{12}\ ]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co	29(1)	30(1)	28(1)	-8(1)	5(1)	-15(1)
N1	32(1)	35(1)	32(1)	-11(1)	7(1)	-18(1)
N2	27(1)	36(1)	30(1)	-9(1)	5(1)	-15(1)
N3	32(1)	32(1)	30(1)	-10(1)	5(1)	-14(1)
N4	34(1)	32(1)	30(1)	-8(1)	6(1)	-17(1)
C1	44(1)	35(1)	30(1)	-9(1)	9(1)	-22(1)
C2	46(2)	41(1)	35(1)	-8(1)	12(1)	-23(1)
C3	40(1)	48(2)	38(1)	-15(1)	15(1)	-26(1)
C4	34(1)	42(1)	32(1)	-13(1)	6(1)	-21(1)

C5	30(1)	45(2)	33(1)	-14(1)	6(1)	-19(1)
C6	33(1)	43(1)	32(1)	-5(1)	7(1)	-16(1)
C7	37(2)	73(2)	40(2)	-19(2)	5(1)	-17(1)
C8	54(2)	74(2)	39(2)	-20(2)	11(1)	-12(2)
C9	35(2)	57(2)	54(2)	-8(2)	16(1)	-10(1)
C10	35(2)	80(2)	86(3)	-40(2)	17(2)	-28(2)
C11	38(2)	74(2)	69(2)	-37(2)	14(1)	-29(2)
C12	28(1)	42(1)	33(1)	-11(1)	4(1)	-15(1)
C13	30(1)	44(2)	40(1)	-11(1)	7(1)	-10(1)
C14	33(1)	35(1)	39(1)	-9(1)	5(1)	-12(1)
C15	28(1)	32(1)	34(1)	-9(1)	2(1)	-14(1)
C16	34(1)	32(1)	31(1)	-9(1)	3(1)	-17(1)
C17	32(1)	31(1)	33(1)	-11(1)	9(1)	-12(1)
C18	48(2)	42(2)	41(2)	-12(1)	-1(1)	-22(1)
C19	54(2)	47(2)	33(1)	-10(1)	-3(1)	-13(1)
C20	55(2)	32(1)	37(2)	-6(1)	18(1)	-11(1)
C21	45(2)	40(2)	67(2)	-10(1)	14(2)	-24(1)
C22	35(1)	42(2)	56(2)	-8(1)	2(1)	-18(1)
C23	35(1)	31(1)	30(1)	-7(1)	4(1)	-16(1)
C24	41(1)	36(1)	28(1)	-8(1)	7(1)	-16(1)
C25	40(1)	39(1)	30(1)	-13(1)	8(1)	-17(1)
C26	33(1)	36(1)	33(1)	-15(1)	8(1)	-18(1)
C27	33(1)	33(1)	36(1)	-13(1)	6(1)	-18(1)
C28	31(1)	33(1)	30(1)	-8(1)	4(1)	-12(1)
C29	41(2)	41(1)	43(2)	-16(1)	10(1)	-22(1)
C30	36(1)	50(2)	45(2)	-14(1)	10(1)	-23(1)
C31	33(1)	50(2)	39(2)	-13(1)	8(1)	-11(1)
C32	44(2)	53(2)	69(2)	-37(2)	12(1)	-15(1)
C33	38(2)	48(2)	62(2)	-28(1)	10(1)	-21(1)
C34	31(1)	32(1)	37(1)	-10(1)	7(1)	-17(1)
C35	31(1)	38(1)	46(2)	-7(1)	7(1)	-13(1)
C36	37(1)	36(1)	42(2)	-2(1)	2(1)	-13(1)
C37	37(1)	33(1)	35(1)	-8(1)	3(1)	-17(1)
C38	41(1)	34(1)	34(1)	-10(1)	6(1)	-18(1)
C39	39(1)	39(1)	33(1)	-7(1)	7(1)	-18(1)
C40	101(3)	46(2)	38(2)	-9(1)	-3(2)	-35(2)

C41	112(3)	45(2)	50(2)	-5(2)	-7(2)	-39(2)
C42	61(2)	55(2)	36(2)	1(1)	0(1)	-31(2)
C43	47(2)	62(2)	35(2)	-14(1)	2(1)	-22(1)
C44	48(2)	45(2)	43(2)	-16(1)	5(1)	-16(1)
Cl1	41(1)	61(1)	57(1)	-38(1)	5(1)	-19(1)
C45	41(2)	31(3)	29(3)	-5(3)	3(2)	-18(1)
C46	46(2)	47(2)	35(2)	-18(2)	9(2)	-26(2)
Cl2	48(1)	80(1)	55(1)	-37(1)	18(1)	-41(1)
Cl1'	114(7)	163(8)	91(5)	-58(5)	19(4)	-101(7)
C45'	41(2)	31(3)	29(3)	-5(3)	3(2)	-18(1)
C46'	113(16)	82(14)	79(13)	-51(11)	9(10)	-63(15)
Cl2'	100(6)	269(13)	195(10)	-183(10)	53(6)	-89(7)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **3**.

	x	y	z	U(eq)
H2A	10218	3462	-450	50
H3A	12142	1558	243	49
H7A	12547	-1351	440	63
H8A	14388	-2139	-226	74
H9A	16101	-2174	456	69
H10A	15999	-1504	1816	76
H11A	14184	-746	2500	67
H13A	13179	-3189	3005	50
H14A	12168	-4188	4481	46
H18A	12040	-3735	6456	52
H19A	12642	-5754	7830	59
H20A	11519	-6958	8073	57
H21A	9798	-6142	6953	63
H22A	9161	-4102	5587	56
H24A	8761	-2144	6645	44
H25A	7090	-12	6209	44
H29A	5025	1030	4455	48
H30A	3252	1748	5203	53
H31A	2869	3331	5848	53
H32A	4245	4222	5711	63
H33A	5992	3562	4900	56
H35A	5194	4076	2631	51
H36A	5880	4803	859	52
H40A	7634	5798	270	74
H41A	6944	7567	-1338	84
H42A	6796	7285	-2884	65
H43A	7235	5242	-2806	59
H44A	7886	3474	-1204	56
H46A	7457	-552	1585	48
H46B	8170	-832	1328	92

Table 6. Torsion angles [°] for **3**.

C45'-Co-N1-C1	81.7(18)	N2-Co-N4-C34	-88.0(8)
C45-Co-N1-C1	80.7(4)	C45'-Co-N4-C37	-78.5(10)
N3-Co-N1-C1	-100.4(4)	C45-Co-N4-C37	-71.0(3)
N2-Co-N1-C1	172.2(2)	N1-Co-N4-C37	22.7(2)
N4-Co-N1-C1	-13.2(2)	N3-Co-N4-C37	-171.8(2)
C45'-Co-N1-C4	-93.9(18)	N2-Co-N4-C37	106.0(8)
C45-Co-N1-C4	-94.9(4)	C4-N1-C1-C38	175.9(2)
N3-Co-N1-C4	84.0(4)	Co-N1-C1-C38	-0.4(4)
N2-Co-N1-C4	-3.4(2)	C4-N1-C1-C2	-4.2(3)
N4-Co-N1-C4	171.2(2)	Co-N1-C1-C2	179.41(17)
C45'-Co-N2-C15	-70.1(10)	N1-C1-C2-C3	2.2(3)
C45-Co-N2-C15	-77.6(3)	C38-C1-C2-C3	-177.9(3)
N1-Co-N2-C15	-171.3(2)	C1-C2-C3-C4	0.7(3)
N3-Co-N2-C15	23.1(2)	C1-N1-C4-C5	-166.9(2)
N4-Co-N2-C15	105.4(8)	Co-N1-C4-C5	9.5(4)
C45'-Co-N2-C12	92.2(10)	C1-N1-C4-C3	4.6(3)
C45-Co-N2-C12	84.7(3)	Co-N1-C4-C3	-179.00(17)
N1-Co-N2-C12	-9.0(2)	C2-C3-C4-C5	168.2(3)
N3-Co-N2-C12	-174.6(2)	C2-C3-C4-N1	-3.4(3)
N4-Co-N2-C12	-92.3(8)	N1-C4-C5-C12	-3.1(4)
C45'-Co-N3-C23	81.4(17)	C3-C4-C5-C12	-173.4(2)
C45-Co-N3-C23	82.3(4)	N1-C4-C5-C6	171.1(2)
N1-Co-N3-C23	-96.6(4)	C3-C4-C5-C6	0.8(4)
N2-Co-N3-C23	-9.1(2)	C4-C5-C6-C7	-84.2(3)
N4-Co-N3-C23	176.4(2)	C12-C5-C6-C7	90.2(3)
C45'-Co-N3-C26	-99.6(17)	C4-C5-C6-C11	96.5(3)
C45-Co-N3-C26	-98.6(4)	C12-C5-C6-C11	-89.0(3)
N1-Co-N3-C26	82.5(4)	C11-C6-C7-C8	0.5(5)
N2-Co-N3-C26	170.0(2)	C5-C6-C7-C8	-178.8(3)
N4-Co-N3-C26	-4.6(2)	C6-C7-C8-C9	-1.0(5)
C45'-Co-N4-C34	87.5(10)	C7-C8-C9-C10	1.0(5)
C45-Co-N4-C34	94.9(3)	C8-C9-C10-C11	-0.6(5)
N1-Co-N4-C34	-171.3(2)	C9-C10-C11-C6	0.1(5)
N3-Co-N4-C34	-5.8(2)	C7-C6-C11-C10	0.0(5)

C5-C6-C11-C10	179.2(3)	C15-C16-C23-C24	-169.3(2)
C15-N2-C12-C5	-177.6(2)	C17-C16-C23-C24	5.5(4)
Co-N2-C12-C5	17.1(4)	C26-N3-C23-C16	175.5(2)
C15-N2-C12-C13	2.8(3)	Co-N3-C23-C16	-5.3(4)
Co-N2-C12-C13	-162.55(18)	C26-N3-C23-C24	-4.2(3)
C4-C5-C12-N2	-10.6(4)	Co-N3-C23-C24	175.01(16)
C6-C5-C12-N2	175.1(2)	C16-C23-C24-C25	-177.1(2)
C4-C5-C12-C13	169.0(3)	N3-C23-C24-C25	2.6(3)
C6-C5-C12-C13	-5.2(4)	C23-C24-C25-C26	0.1(3)
N2-C12-C13-C14	-0.7(3)	C23-N3-C26-C27	-170.5(2)
C5-C12-C13-C14	179.6(3)	Co-N3-C26-C27	10.3(3)
C12-C13-C14-C15	-1.5(3)	C23-N3-C26-C25	4.3(3)
C12-N2-C15-C16	169.5(2)	Co-N3-C26-C25	-174.95(16)
Co-N2-C15-C16	-25.0(3)	C24-C25-C26-C27	172.0(2)
C12-N2-C15-C14	-3.7(3)	C24-C25-C26-N3	-2.8(3)
Co-N2-C15-C14	161.77(17)	N3-C26-C27-C34	-4.9(4)
C13-C14-C15-N2	3.4(3)	C25-C26-C27-C34	-178.9(2)
C13-C14-C15-C16	-169.9(2)	N3-C26-C27-C28	167.7(2)
N2-C15-C16-C23	4.6(4)	C25-C26-C27-C28	-6.4(4)
C14-C15-C16-C23	177.0(2)	C26-C27-C28-C33	108.3(3)
N2-C15-C16-C17	-170.2(2)	C34-C27-C28-C33	-78.9(3)
C14-C15-C16-C17	2.1(4)	C26-C27-C28-C29	-71.6(3)
C23-C16-C17-C22	74.7(3)	C34-C27-C28-C29	101.2(3)
C15-C16-C17-C22	-110.3(3)	C33-C28-C29-C30	0.0(4)
C23-C16-C17-C18	-106.2(3)	C27-C28-C29-C30	179.9(2)
C15-C16-C17-C18	68.8(3)	C28-C29-C30-C31	-1.0(4)
C22-C17-C18-C19	-0.1(4)	C29-C30-C31-C32	0.7(4)
C16-C17-C18-C19	-179.2(2)	C30-C31-C32-C33	0.6(5)
C17-C18-C19-C20	0.5(4)	C29-C28-C33-C32	1.3(4)
C18-C19-C20-C21	-0.2(4)	C27-C28-C33-C32	-178.6(3)
C19-C20-C21-C22	-0.4(5)	C31-C32-C33-C28	-1.6(5)
C18-C17-C22-C21	-0.5(4)	C37-N4-C34-C27	-179.7(2)
C16-C17-C22-C21	178.6(3)	Co-N4-C34-C27	11.9(4)
C20-C21-C22-C17	0.7(5)	C37-N4-C34-C35	1.2(3)
C15-C16-C23-N3	11.0(4)	Co-N4-C34-C35	-167.23(17)
C17-C16-C23-N3	-174.2(2)	C26-C27-C34-N4	-6.5(4)

C28-C27-C34-N4	-179.1(2)
C26-C27-C34-C35	172.5(2)
C28-C27-C34-C35	0.0(4)
N4-C34-C35-C36	0.6(3)
C27-C34-C35-C36	-178.6(3)
C34-C35-C36-C37	-2.1(3)
C34-N4-C37-C38	171.5(2)
Co-N4-C37-C38	-19.9(4)
C34-N4-C37-C36	-2.5(3)
Co-N4-C37-C36	166.14(18)
C35-C36-C37-N4	2.9(3)
C35-C36-C37-C38	-171.1(3)
N1-C1-C38-C37	11.4(4)
C2-C1-C38-C37	-168.5(3)
N1-C1-C38-C39	-171.5(2)
C2-C1-C38-C39	8.6(4)
N4-C37-C38-C1	-0.8(4)
C36-C37-C38-C1	172.3(3)
N4-C37-C38-C39	-177.9(2)
C36-C37-C38-C39	-4.7(4)
C1-C38-C39-C40	-108.4(3)
C37-C38-C39-C40	68.8(4)
C1-C38-C39-C44	70.8(3)
C37-C38-C39-C44	-112.0(3)
C44-C39-C40-C41	-0.2(5)
C38-C39-C40-C41	179.0(3)
C39-C40-C41-C42	-1.2(6)
C40-C41-C42-C43	1.8(6)
C41-C42-C43-C44	-1.1(5)
C42-C43-C44-C39	-0.3(4)
C40-C39-C44-C43	0.9(4)
C38-C39-C44-C43	-178.3(3)
C45'-Co-C45-C46	51(14)
N1-Co-C45-C46	-136.9(10)
N3-Co-C45-C46	43.4(11)
N2-Co-C45-C46	132.9(10)
N4-Co-C45-C46	-47.4(10)
C45'-Co-C45-Cl1	-128(15)
N1-Co-C45-Cl1	44.4(6)
N3-Co-C45-Cl1	-135.4(5)
N2-Co-C45-Cl1	-45.9(6)
N4-Co-C45-Cl1	133.8(5)
Cl1-C45-C46-Cl2	-179.0(3)
Co-C45-C46-Cl2	2.2(13)
C45-Co-C45'-C46'	32(9)
N1-Co-C45'-C46'	24(6)
N3-Co-C45'-C46'	-156(6)
N2-Co-C45'-C46'	-67(6)
N4-Co-C45'-C46'	114(6)
C45-Co-C45'-Cl1'	-135(18)
N1-Co-C45'-Cl1'	-143(3)
N3-Co-C45'-Cl1'	37(3)
N2-Co-C45'-Cl1'	126(3)
N4-Co-C45'-Cl1'	-53(3)
Cl1'-C45'-C46'-Cl2'	175.1(18)
Co-C45'-C46'-Cl2'	8(8)
C45'-C46'-Cl2'-Cl2'#1	-101(4)

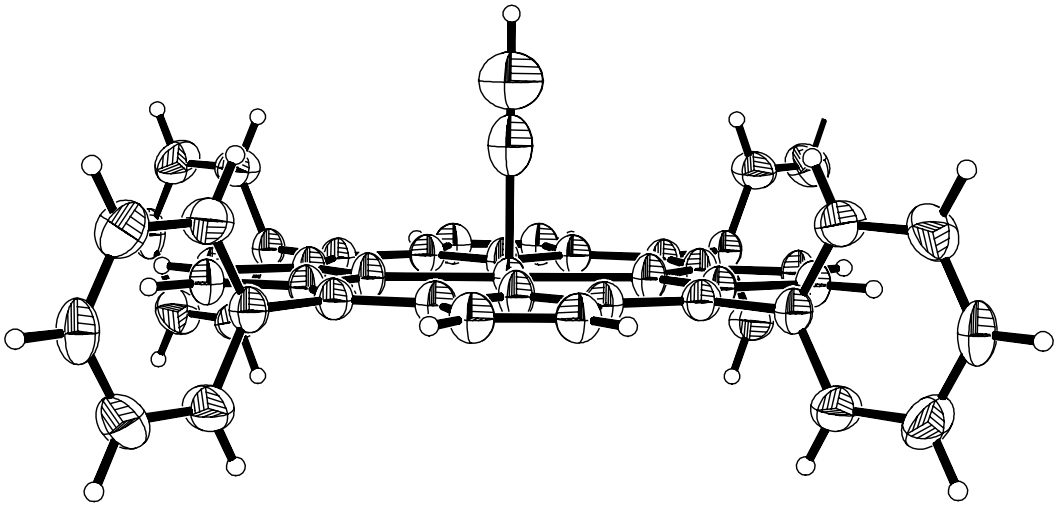
Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y,-z

X-Ray report for 4

CRYSTAL STRUCTURE REPORT

$C_{46}\ H_{29}\ Co_{1}\ N_{4}$



Report prepared for:

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September 15, 2005

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Data collection

A crystal (approximate dimensions 0.2 x 0.2 x 0.2 mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Siemens SMART Platform CCD diffractometer for a data collection at 173(2) K.[1] A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 96 reflections. The data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 30 seconds and a detector distance of 4.9 cm. A randomly oriented region of reciprocal space was surveyed to the extent of one sphere and to a resolution of 0.84 Å. Four major sections of frames were collected with 0.30º steps in ω at four different ϕ settings and a detector position of -28º in 2θ. The intensity data were corrected for absorption and decay (SADABS).[2] Final cell constants were calculated from the xyz centroids of 3191 strong reflections from the actual data collection after integration (SAINT).[3] Please refer to Table 1 for additional crystal and refinement information.

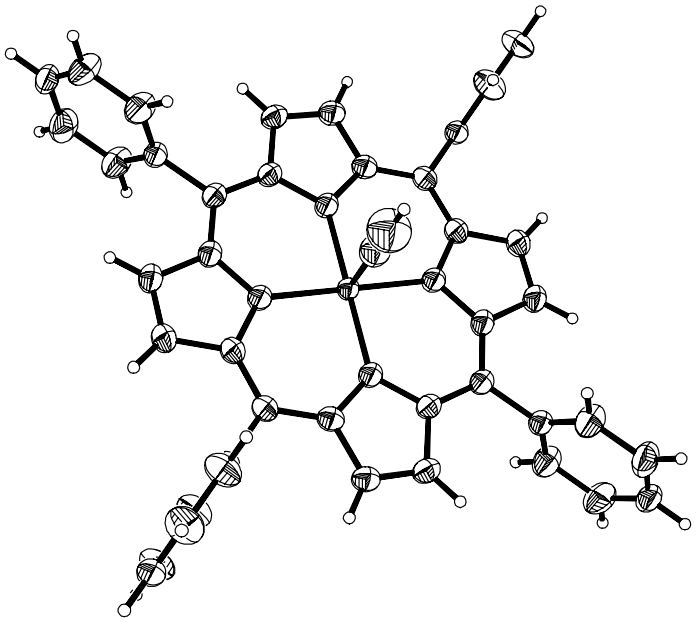
Structure solution and refinement

The structure was solved using SHELXS-97 [4] and refined using SHELXL-97.[4] The space group I4/m was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0360$ and $wR2 = 0.1134$ (F^2, all data).

The structure was solved in I4/m, but other suitable solutions were obtained with I4 and I-4. This space group was chosen because it yielded the most reasonable solution for the acetylide portion for bond lengths and thermal ellipsoids. The solution would like the structure to be a diacetylide via symmetry operations, but we believe that it is a monoacetylide cobalt coordination because Co^{IV} is not a viable oxidation state, no lithium counter ion was observed in the structure, ^1H NMR suggests monoacetylide in comparison to the (Krattringer 1996) diacetylide NMR, and ESI-MS data supports the monoacetylide. As a result, the acetylide moiety was refined for partial occupancy. The unit cell and crystal packing (intermolecular distances are significant) do not provide any intermolecular forces directing the position of the acetylide. As a result, it could be in one of two confirmations "up" or "down". It is this up/down occupancy that was refined. The refinement yielded 61% in the up confirmation and 39% in the down. Also the cobalt atom was located on a 4-fold axis with mirror plane which contributed to some of the refinement difficulties mentioned above.

Structure description

The structure is the one suggested.



Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, S146 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1)include Joe Fritsch as a coauthor or 2)acknowledge Joe Fritsch, Victor G. Young, Jr., and the X-Ray Crystallographic Laboratory.

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[1] SMART V5.054, Bruker Analytical X-ray Systems, Madison, WI (2001).

[2] An empirical correction for absorption anisotropy, R. Blessing, *Acta Cryst.* **A51**, 33-38 (1995).

[3] SAINT+ V6.45, Bruker Analytical X-Ray Systems, Madison, WI (2003).

[4] SHELXTL V6.14, Bruker Analytical X-Ray Systems, Madison, WI (2000).

Some equations of interest:

$$R_{int} = \Sigma\, |F_o^2 - < F_o^2 >| \,/\, \Sigma |F_o^2|$$

$$R_1 = \Sigma ||F_o| - |F_c|| \,/\, \Sigma |F_o|$$

$$wR2 = [\Sigma [w(F_o^2 - F_c^2)^2] \,/\, \Sigma\, [w(F_o^2)^2]]^{1/2}$$

$$\text{where } w = q \,/\, [\sigma^2 (F_o^2) + (a*P)^2 + b*P + d + e*\sin(\theta)]$$

$$\text{GooF} = S = [\Sigma [w(F_o^2 - F_c^2)^2] \,/\, (n-p)]^{1/2}$$

Table 1. Crystal data and structure refinement for **4**.

Identification code	05250i4m	
Empirical formula	C46 H29 Co1 N4	
Formula weight	696.17	
Temperature	173(2) K	
Wavelength	0.71069 Å	
Crystal system	Tetragonal	
Space group	I4/m	
Unit cell dimensions	a = 13.5200(9) Å	α = 90 °
	b = 13.5200 Å	β = 90 °
	c = 9.7890(7) Å	γ = 90 °
Volume	1789.3(13) Å^3	
Z	2	
Density (calculated)	1.293 Mg/m^3	
Absorption coefficient	0.518 mm^{-1}	
F(000)	720	
Crystal color, morphology	purple, block	
Crystal size	0.2 x 0.2 x 0.2 mm^3	
Theta range for data collection	2.13 to 25.07°	
Index ranges	$-16 \le h \le 16$, $-16 \le k \le 16$, $-11 \le l \le 11$	
Reflections collected	7990	
Independent reflections	847 [R(int) = 0.0257]	
Observed reflections	820	
Completeness to theta = 25.07°	100.0%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.902 and 0.899	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	847 / 1 / 76	
Goodness-of-fit on F^2	1.254	
Final R indices [I>2sigma(I)]	R1 = 0.0360, wR2 = 0.1126	
R indices (all data)	R1 = 0.0370, wR2 = 0.1134	
Largest diff. peak and hole	0.258 and -0.536 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **4**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Co1	0	0	0	25(1)
N1	370(2)	-1415(2)	0	32(1)
C1	1312(2)	-1810(2)	0	30(1)
C2	1262(2)	-2873(2)	0	34(1)
C3	302(2)	-3124(2)	0	35(1)
C4	-258(2)	-2222(2)	0	31(1)
C5	-1283(2)	-2189(2)	0	29(1)
C6	-1844(2)	-3151(2)	0	30(1)
C7	-2102(2)	-3600(2)	-1213(3)	44(1)
C8	-2622(2)	-4487(2)	-1212(3)	50(1)
C9	-2884(2)	-4924(2)	0	41(1)
C10	0	0	2070(30)	52(4)
C11	0	0	3030(30)	77(6)
C10'	0	0	-1720(30)	52(4)
C11'	0	0	-2610(30)	77(6)

Table 3. Bond lengths [Å] and angles [°] for **4**.

Co(1)-C(10')#1	1.69(3)	C(2)-C(3)	1.341(5)
Co(1)-C(10')	1.69(3)	C(2)-H(6A)	0.9500
Co(1)-N(1)#2	1.977(3)	C(3)-C(4)	1.435(4)
Co(1)-N(1)#3	1.977(3)	C(3)-H(7A)	0.9500
Co(1)-N(1)#1	1.977(3)	C(4)-C(5)	1.387(4)
Co(1)-N(1)	1.977(3)	C(5)-C(1)#3	1.384(4)
Co(1)-C(10)	2.02(3)	C(5)-C(6)	1.505(4)
Co(1)-C(10)#1	2.02(3)	C(6)-C(7)#4	1.378(3)
N(1)-C(1)	1.381(4)	C(6)-C(7)	1.378(3)
N(1)-C(4)	1.383(4)	C(7)-C(8)	1.390(3)
C(1)-C(5)#2	1.384(4)	C(7)-H(10A)	0.9500
C(1)-C(2)	1.438(4)	C(8)-C(9)	1.372(3)
		C(8)-H(11A)	0.9500
		C(9)-C(8)#4	1.372(3)

C(9)-H(9A)	0.9500	C(10')#1-Co(1)-C(10)	0.0
C(10)-C(11)	0.942(12)	C(10')-Co(1)-C(10)	180.000(1)
C(11)-H(11)	0.9500	N(1)#2-Co(1)-C(10)	90.0
C(10')-C(11')	0.8727	N(1)#3-Co(1)-C(10)	90.0
C(11')-H(11')	0.9500	N(1)#1-Co(1)-C(10)	90.0
		N(1)-Co(1)-C(10)	90.0
C(10')#1-Co(1)-C(10')	180.0	C(10')#1-Co(1)-C(10)#1	180.0
C(10')#1-Co(1)-N(1)#2	90.0	C(10')-Co(1)-C(10)#1	0.0
C(10')-Co(1)-N(1)#2	90.0	N(1)#2-Co(1)-C(10)#1	90.0
C(10')#1-Co(1)-N(1)#3	90.0	N(1)#3-Co(1)-C(10)#1	90.0
C(10')-Co(1)-N(1)#3	90.0	N(1)#1-Co(1)-C(10)#1	90.0
N(1)#2-Co(1)-N(1)#3	180.0	N(1)-Co(1)-C(10)#1	90.0
C(10')#1-Co(1)-N(1)#1	90.0	C(10)-Co(1)-C(10)#1	180.0
C(10')-Co(1)-N(1)#1	90.0	C(1)-N(1)-C(4)	105.1(2)
N(1)#2-Co(1)-N(1)#1	90.0	C(1)-N(1)-Co(1)	127.4(2)
N(1)#3-Co(1)-N(1)#1	90.0	C(4)-N(1)-Co(1)	127.5(2)
C(10')#1-Co(1)-N(1)	89.998(1)	N(1)-C(1)-C(5)#2	126.3(3)
C(10')-Co(1)-N(1)	90.0	N(1)-C(1)-C(2)	110.1(3)
N(1)#2-Co(1)-N(1)	90.0	C(5)#2-C(1)-C(2)	123.7(3)
N(1)#3-Co(1)-N(1)	90.0	C(3)-C(2)-C(1)	107.4(3)
N(1)#1-Co(1)-N(1)	180.0		
C(3)-C(2)-H(6A)	126.3	C(6)-C(7)-H(10A)	119.8
C(1)-C(2)-H(6A)	126.3	C(8)-C(7)-H(10A)	119.8
C(2)-C(3)-C(4)	107.2(3)	C(9)-C(8)-C(7)	120.1(3)
C(2)-C(3)-H(7A)	126.4	C(9)-C(8)-H(11A)	119.9
C(4)-C(3)-H(7A)	126.4	C(7)-C(8)-H(11A)	119.9
N(1)-C(4)-C(5)	126.0(3)	C(8)#4-C(9)-C(8)	119.7(3)
N(1)-C(4)-C(3)	110.3(3)	C(8)#4-C(9)-H(9A)	120.1
C(5)-C(4)-C(3)	123.7(3)	C(8)-C(9)-H(9A)	120.1
C(1)#3-C(5)-C(4)	122.8(3)	C(11)-C(10)-Co(1)	180.000(2)
C(1)#3-C(5)-C(6)	118.8(3)	C(10)-C(11)-H(11)	180.0
C(4)-C(5)-C(6)	118.4(3)	C(11')-C(10')-Co(1)	180.0
C(7)#4-C(6)-C(7)	119.0(3)	C(10')-C(11')-H(11')	180.0
C(7)#4-C(6)-C(5)	120.52(15)		
C(7)-C(6)-C(5)	120.52(15)		
C(6)-C(7)-C(8)	120.5(2)		

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z #2 -y,x,z #3 y,-x,-z #4 x,y,-z

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **4**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U_{11} + ... + 2\ h\ k\ a^*\ b^*\ U_{12}\ ]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co1	21(1)	21(1)	32(1)	0	0	0
N1	25(1)	25(1)	47(2)	0	0	0(1)
C1	28(2)	27(1)	35(2)	0	0	4(1)
C2	33(2)	27(2)	42(2)	0	0	5(1)
C3	35(2)	25(2)	44(2)	0	0	0(1)
C4	32(2)	24(1)	36(2)	0	0	-2(1)
C5	30(2)	27(2)	31(2)	0	0	-4(1)
C6	28(2)	25(1)	36(2)	0	0	-1(1)
C7	54(2)	42(1)	36(1)	1(1)	-2(1)	-13(1)
C8	56(2)	42(1)	51(2)	-12(1)	-5(1)	-13(1)
C9	32(2)	25(2)	68(2)	0	0	-3(1)
C10	40(2)	40(2)	76(13)	0	0	0
C11	83(4)	83(4)	66(17)	0	0	0
C10'	40(2)	40(2)	76(13)	0	0	0
C11'	83(4)	83(4)	66(17)	0	0	0

Table 5. Hydrogen coordinates ($x\ 10^4$) and isotropic displacement parameters ($Å^2\ x\ 10^3$) for **4**.

	x	y	z	U(eq)
H6A	1808	-3315	0	41
H7A	42	-3777	0	42
H10A	-1925	-3300	-2056	53
H11A	-2795	-4792	-2053	60

H9A	-3246	-5526	0	50
H11	0	0	4000	93
H11'	0	0	-3584	93

Table 6. Torsion angles [°] for **4**.

C10'#1-Co1-N1-C1	-90.0	N1-C4-C5-C1#3	0.0
C10'-Co1-N1-C1	90.0	C3-C4-C5-C1#3	180.0
N1#2-Co1-N1-C1	0.0	N1-C4-C5-C6	180.0
N1#3-Co1-N1-C1	180.0	C3-C4-C5-C6	0.0
N1#1-Co1-N1-C1	180.0	C1#3-C5-C6-C7#4	-90.1(3)
C10-Co1-N1-C1	-90.0	C4-C5-C6-C7#4	89.9(3)
C10#1-Co1-N1-C1	90.0	C1#3-C5-C6-C7	90.1(3)
C10'#1-Co1-N1-C4	90.0	C4-C5-C6-C7	-89.9(3)
C10'-Co1-N1-C4	-90.0	C7#4-C6-C7-C8	0.4(5)
N1#2-Co1-N1-C4	180.0	C5-C6-C7-C8	-179.9(3)
N1#3-Co1-N1-C4	0.0	C6-C7-C8-C9	0.2(4)
N1#1-Co1-N1-C4	0.0	C7-C8-C9-C8#4	-0.8(6)
C10-Co1-N1-C4	90.0	C10'#1-Co1-C10-C11	0(100)
C10#1-Co1-N1-C4	-90.0	C10'-Co1-C10-C11	0.0
C4-N1-C1-C5#2	180.0	N1#2-Co1-C10-C11	0(100)
Co1-N1-C1-C5#2	0.0	N1#3-Co1-C10-C11	0(100)
C4-N1-C1-C2	0.0	N1#1-Co1-C10-C11	0(100)
Co1-N1-C1-C2	180.0	N1-Co1-C10-C11	0(100)
N1-C1-C2-C3	0.0	C10#1-Co1-C10-C11	0(100)
C5#2-C1-C2-C3	180.0	C10'#1-Co1-C10'-C11'	0(100)
C1-C2-C3-C4	0.0	N1#2-Co1-C10'-C11'	0(100)
C1-N1-C4-C5	180.0	N1#3-Co1-C10'-C11'	0(100)
Co1-N1-C4-C5	0.0	N1#1-Co1-C10'-C11'	0(100)
C1-N1-C4-C3	0.0	N1-Co1-C10'-C11'	0(100)
Co1-N1-C4-C3	180.0	C10-Co1-C10'-C11'	0.0
C2-C3-C4-N1	0.0	C10#1-Co1-C10'-C11'	0(100)
C2-C3-C4-C5	180.0		

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z #2 -y,x,z #3 y,-x,-z #4 x,y,-z