The signal assignment follows from the comparison of the spectra of $[CpCrCl_2]_2$ (**13**) (δ_{306} (^{13}C) = 103.6[S1]), $[(MeCp)CrCl_2]_2$[10] (**14**), and $[(t\text{-}BuCp)CrCl_2]_2$ (**8**). On passing from the Cp to the MeCp derivative (**13** → **14**) the signal at 103.6 ppm is replaced by a 1/2/2 pattern. The signals of C3/4 and C2/5 are distinguished By the fact that either $|\delta(C1)| < |\delta(C3/4)| < |\delta(C2/5)|$ or the inverted sequence may be observed.[14] In addition, a strongly shifted broad signal for CH_3 of **14** is observed. The signal pattern in the spectrum of **8** is similar to that of **14**. However, the signal separation is larger for two reasons: (i) The temperature is lower. (ii) The perturbation of the spin distribution on the Cp ligand by

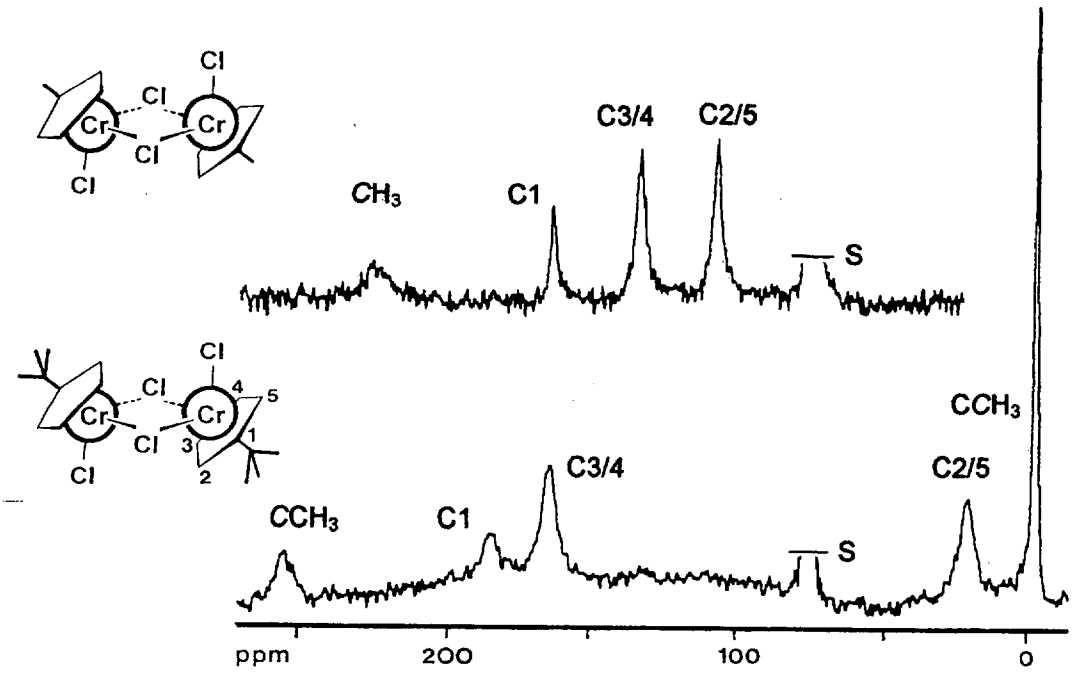

Figure S1. ^{13}C NMR spectra of $[(MeCp)CrCl_2]_2$ at 337 K and $[(t\text{-}BuCp)CrCl_2]_2$ at 305 K both dissolved in $CDCl_3$ (S).

by analogy to substituted chromocenes and vanadocenes[10] the signals of C1 –5 of **8** and other compounds of the type $[(R_nCp)CrX_2]_2$ are expected at low frequency relative to the corresponding signals of suitable diamagnetic reference compounds. The reason is that negative spin is induced on the Cp ligand by π polarization.[10] In the present case σ delocalization (and some dipolar shift contribution) move all signals considerably to high frequency; similar examples are ferrocenium ions[15] and low-spin manganocenes.[S2] Hence, if pure π polarization were operating, the signals of C1-5 of **8** would appear at the low frequency side and the sequence would be $|\delta(C1)| < |\delta(C3/4)| < |\delta(C2/5)|$. This is important for the distinction of H3/4 and H2/5 (see Experimental Section), because the sequence of $|\delta(H3/4)|$ and $|\delta(H2/5)|$ is always opposite to that of $|\delta(C1)|$, $|\delta(C3/4)|$, and $|\delta(C2/5)|$ provided pure π delocalization determines the signal shifts.

(S1) Köhler, F. H.; Ackermann, K.; Sedlmair, J. *Z. Naturforsch. B* **1983**, *38*, 1406-1411.

(S2) Hebendanz, N.; Köhler, F. H.; Müller, G.; Riede, J. *J. Am. Chem. Soc.* **1986**, *108*, 3281-3289.

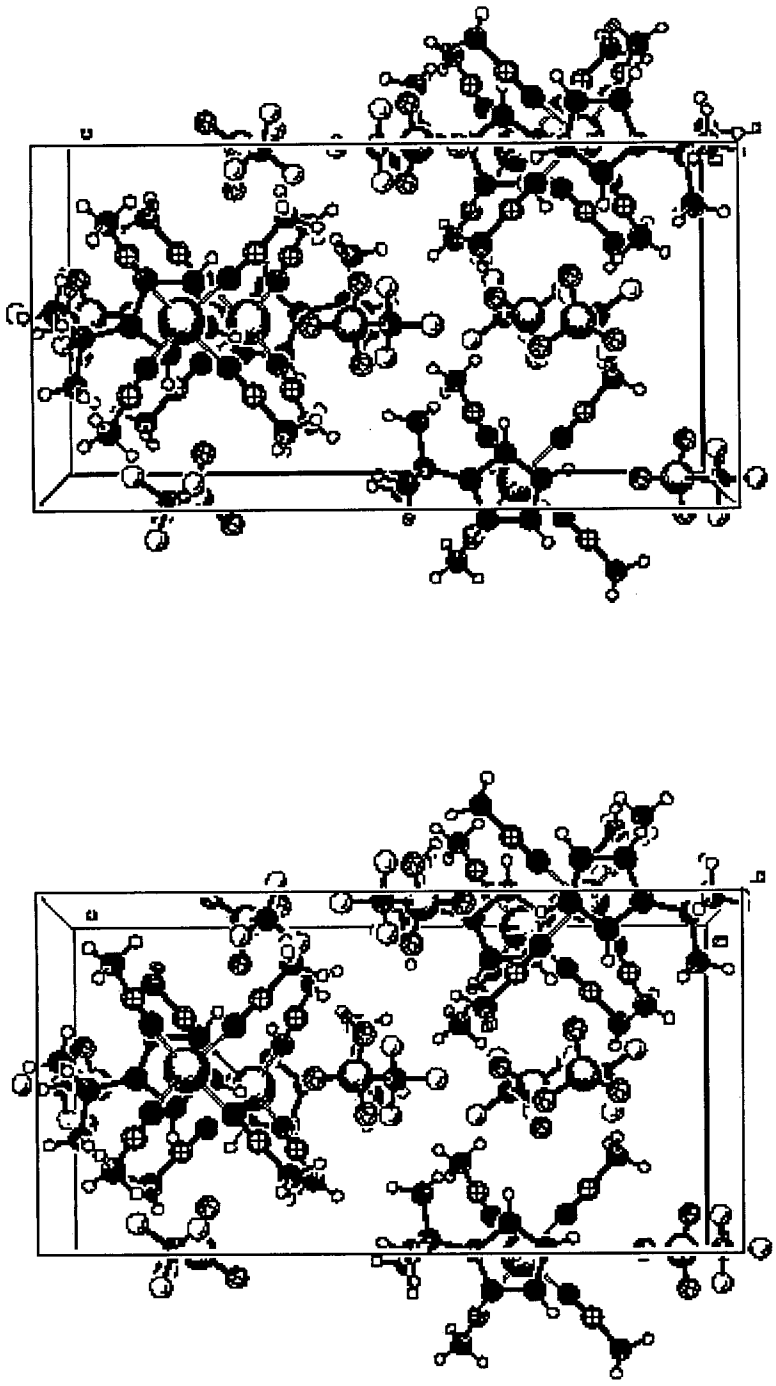

Figure SI 2. Stereo view of the unit cell of $\mathbf{10}^{2+}[CF_3SO_3]^-_2$

for **HAIA 4028-143**

Crystal Data

Empirical Formula	C17 H25 Cr N4, 2(C F3 O3 S)		
Formula Weight	635.57		
Crystal System	Orthorhombic		
Space group	P212121 (No. 19)		
a, b, c [Å]	10.7930(4)	11.9055(6)	20.9211(10)
alpha, beta, gamma [deg]	90	90	90
V [Ang**3]	2688.3(2)		
Z	4		
Mosaicity	1.019(2)		
D(obs), D(calc) [g/cm**3]	0.000, 1.570		
F(000) [Electrons]	1300		
Mu(MoKa) [/mm]	0.664		
Crystal Size [mm]	0.05 x	0.18 x	0.23

Data Collection

Temperature (K)	143		
Radiation [Å]	Drehanode	50 / 60	MoKa 0.71073
Theta Min-Max [Deg]	1.95, 25.64		
Kollimator [Nr.;mm]	0540.353; 0.61		
Device	Nonius Kappa CCD		
Scan Characteristics set 1 [mm; Deg; Deg]:			
Dx = 40;	Phi(start) = -314.5;	Delta-Phi = 1	
Scan Type	Phi movement mode		
Theta offset [Deg]	9.84		
Scan Characteristics set 2 [mm; Deg; Deg]:			
Dx = 40;	Omega(start) = -210.0;	Delta-Omega = 1	
Scan Type	Omega movement mode		
Theta offset [Deg]	-9.84		
Scan Characteristics set 1 [mm; Deg; Deg]:			
Dx = 40;	Omega(start) = 128.4;	Delta-Omega = 1	
Scan Type	Omega movement mode		
Theta offset [Deg]	-8.9		
Exposure time [s] x repetition	60 x 2		
Dataset	-12: 13 ; -12: 14 ; -23: 25		
Resolution [min; max]	25.0; 0.82		
Completeness of the data set	100.0%		
Tot., Uniq. Data, R(int)	13855,	5081,	0.053
Observed data [I > 2.0 sigma(I)]	4371		

Refinement

Nref, Npar	5081, 344		
R [4371 data]	0.0561		
R, wR, S [all data]	0.0705,	0.1048,	1.100
Weighting Scheme : w = 1 / [sigma^2(Fo^2)+(a*P)^2+b*P]			
with a: 0.0284; b: 3.4239; P: [Maximum(0 or Fo^2)+2*Fc^2]/3			
Flack's Parameter	0.47(3)		
Absolute structure cannot be determined reliably			
Max. and Av. Shift/Error	0.00, 0.00		
Min. and Max. resd. dens. [e/Ang^3]	-0.40, 0.67		

Table S2 - Final Coordinates and Equivalent Isotropic Thermal Parameters of the non-Hydrogen atoms for **HAIA 4028-143**

Atom	x	y	z	U(eq) [Å²]
Cr	0.01454(6)	0.10693(5)	0.29232(3)	0.0185(2)
N1	-0.1812(3)	-0.0482(4)	0.36027(18)	0.0210(12)
N2	0.2014(3)	-0.0558(4)	0.36083(19)	0.0237(14)
N3	0.2044(3)	0.0459(4)	0.18381(19)	0.0223(12)
N4	-0.1894(3)	0.0610(4)	0.1889(2)	0.0280(14)
C1	-0.1088(4)	0.0101(4)	0.3387(2)	0.0200(16)
C2	0.1334(4)	0.0068(4)	0.3383(2)	0.0223(16)
C3	0.1324(4)	0.0654(4)	0.2221(2)	0.0197(14)
C4	-0.1122(4)	0.0795(4)	0.2245(2)	0.0233(16)
C5	-0.2734(4)	-0.1224(5)	0.3871(2)	0.0280(16)
C6	0.2904(4)	-0.1341(5)	0.3862(2)	0.0293(18)
C7	0.3020(4)	0.0260(5)	0.1386(3)	0.0343(18)
C8	-0.2891(5)	0.0417(5)	0.1436(3)	0.0387(19)
C11	0.1186(4)	0.2415(4)	0.3440(2)	0.0287(17)
C12	0.1151(5)	0.2682(4)	0.2792(2)	0.0360(17)
C13	-0.0091(6)	0.2794(3)	0.26200(19)	0.0367(16)
C14	-0.0831(4)	0.2586(4)	0.3164(2)	0.0280(17)
C15	-0.0030(5)	0.2370(3)	0.36920(17)	0.0227(11)
C16	-0.0351(4)	0.2331(4)	0.4400(2)	0.0353(14)
C17	0.0379(5)	0.1421(4)	0.4749(2)	0.050(2)
C18	-0.0019(7)	0.3488(4)	0.4668(2)	0.0490(18)
C19	-0.1746(5)	0.2138(5)	0.4501(3)	0.053(2)
S1	0.99884(12)	0.19157(8)	0.04958(4)	0.0221(3)
F1	1.0941(2)	0.3729(3)	-0.00344(13)	0.0355(10)
F2	0.9935(3)	0.26769(19)	-0.06896(9)	0.0307(7)
F3	0.8948(2)	0.3699(3)	-0.00138(13)	0.0356(10)
O1	1.1152(3)	0.1374(3)	0.03652(16)	0.0347(13)
O2	0.9943(4)	0.2500(2)	0.10963(11)	0.0344(9)
O3	0.8900(3)	0.1288(3)	0.03387(17)	0.0389(13)
C9	0.9946(4)	0.3055(3)	-0.00875(16)	0.0223(11)
S2	0.50470(12)	0.25936(9)	0.27999(5)	0.0304(3)
F4	0.5837(4)	0.1146(4)	0.36340(18)	0.0880(16)
F5	0.5681(5)	0.0484(3)	0.27494(19)	0.101(2)
F6	0.4071(4)	0.0826(4)	0.3294(3)	0.166(3)
O4	0.6301(3)	0.2880(4)	0.2680(3)	0.0747(18)
O5	0.4316(5)	0.2459(4)	0.2258(3)	0.099(2)
O6	0.4531(5)	0.3205(4)	0.3307(2)	0.102(3)
C10	0.5122(5)	0.1193(4)	0.3128(2)	0.0383(16)

U(eq) = 1/3 of the trace of the orthogonalized U

Parameters for **HAIA 4028-143**

Atom	x	y	z	U(iso) [Å²]
H51	-0.33480	-0.14110	0.35430	0.0420
H52	-0.31460	-0.08510	0.42300	0.0420
H53	-0.23340	-0.19140	0.40210	0.0420
H61	0.34800	-0.15650	0.35230	0.0440
H62	0.24720	-0.20050	0.40250	0.0440
H63	0.33670	-0.09840	0.42100	0.0440
H71	0.37120	0.07700	0.14740	0.0520
H72	0.27110	0.03940	0.09520	0.0520
H73	0.33040	-0.05190	0.14230	0.0520
H81	-0.33160	-0.02860	0.15430	0.0580
H82	-0.25470	0.03630	0.10030	0.0580
H83	-0.34810	0.10410	0.14550	0.0580
H111	0.19210	0.22820	0.36780	0.0340
H121	0.18460	0.27710	0.25180	0.0430
H131	-0.03890	0.29790	0.22060	0.0440
H141	-0.17110	0.25890	0.31760	0.0340
H171	0.02460	0.14930	0.52100	0.0750
H172	0.12640	0.15050	0.46540	0.0750
H173	0.00970	0.06800	0.46060	0.0750
H181	-0.02800	0.35330	0.51160	0.0740
H182	-0.04430	0.40710	0.44200	0.0740
H183	0.08790	0.36010	0.46410	0.0740
H191	-0.19400	0.21900	0.49570	0.0790
H192	-0.19720	0.13900	0.43430	0.0790
H193	-0.22150	0.27100	0.42660	0.0790

==========

The Temperature Factor has the Form of Exp(-T) Where

T = 8*(Pi**2)*U*(Sin(Theta)/Lambda)**2 for Isotropic Atoms

Atom	U(1,1)	U(2,2)	U(3,3)	U(2,3)	U(1,3)	U(1,2)
Cr	0.0185(3)	0.0171(3)	0.0198(3)	0.0028(2)	-0.0010(3)	0.0002(3)
N1	0.018(2)	0.024(2)	0.021(2)	0.0013(19)	-0.0002(15)	-0.0005(18)
N2	0.022(2)	0.025(3)	0.024(2)	0.006(2)	-0.0010(16)	-0.0008(18)
N3	0.026(2)	0.021(2)	0.020(2)	0.0049(18)	0.0022(17)	-0.0030(17)
N4	0.025(2)	0.030(3)	0.029(2)	0.007(2)	0.0024(18)	-0.0034(18)
C1	0.021(2)	0.020(3)	0.019(3)	0.004(2)	-0.0030(18)	0.004(2)
C2	0.019(2)	0.028(3)	0.020(3)	0.000(2)	0.0011(19)	-0.010(2)
C3	0.026(2)	0.021(3)	0.012(2)	0.005(2)	-0.0016(18)	-0.0052(19)
C4	0.018(2)	0.018(3)	0.034(3)	0.002(2)	0.000(2)	-0.001(2)
C5	0.025(2)	0.031(3)	0.028(3)	0.006(3)	-0.0001(19)	-0.011(2)
C6	0.023(2)	0.031(4)	0.034(3)	0.012(3)	0.001(2)	0.007(2)
C7	0.021(2)	0.045(4)	0.037(3)	0.008(3)	0.010(2)	0.008(2)
C8	0.032(3)	0.053(4)	0.031(3)	0.009(3)	-0.013(2)	-0.008(3)
C11	0.030(3)	0.020(3)	0.036(3)	-0.006(2)	-0.007(2)	-0.004(2)
C12	0.047(3)	0.019(3)	0.042(3)	0.000(2)	0.011(3)	-0.013(2)
C13	0.070(4)	0.015(2)	0.025(2)	0.0037(16)	-0.015(3)	0.005(3)
C14	0.032(3)	0.017(3)	0.035(3)	-0.005(2)	-0.004(2)	0.010(2)
C15	0.027(2)	0.0135(19)	0.0277(19)	0.0007(15)	-0.005(2)	-0.006(3)
C16	0.050(3)	0.026(2)	0.030(2)	-0.004(2)	0.000(2)	-0.005(2)
C17	0.080(5)	0.044(3)	0.026(2)	0.005(2)	-0.008(3)	-0.001(3)
C18	0.076(4)	0.038(3)	0.033(2)	-0.008(2)	0.001(4)	0.000(4)
C19	0.057(4)	0.055(4)	0.047(3)	-0.014(3)	0.024(3)	-0.010(3)
S1	0.0211(5)	0.0250(5)	0.0202(4)	0.0024(4)	-0.0002(6)	0.0002(6)
F1	0.0329(15)	0.034(2)	0.0395(17)	0.0111(15)	-0.0040(12)	-0.0152(15)
F2	0.0382(13)	0.0363(13)	0.0177(10)	-0.0023(9)	0.0026(13)	0.0013(16)
F3	0.0338(15)	0.038(2)	0.0351(17)	0.0026(15)	0.0060(12)	0.0154(15)
O1	0.0300(17)	0.041(3)	0.033(2)	0.0106(19)	0.0033(15)	0.0159(17)
O2	0.0427(17)	0.0401(18)	0.0203(13)	0.0020(12)	0.0011(18)	0.003(2)
O3	0.0337(18)	0.039(3)	0.044(2)	0.008(2)	-0.0100(16)	-0.0147(18)
C9	0.021(2)	0.026(2)	0.0200(18)	0.0006(15)	-0.003(2)	0.001(3)
S2	0.0246(5)	0.0285(6)	0.0380(6)	0.0032(4)	-0.0027(6)	0.0011(6)
F4	0.125(3)	0.077(3)	0.062(2)	0.026(2)	-0.025(2)	0.021(3)
F5	0.192(5)	0.035(2)	0.076(3)	-0.010(2)	0.019(3)	0.028(2)
F6	0.039(2)	0.104(4)	0.354(9)	0.153(5)	-0.005(3)	-0.024(2)
O4	0.031(2)	0.060(3)	0.133(4)	0.037(3)	-0.005(2)	-0.008(2)
O5	0.125(4)	0.065(3)	0.106(4)	0.040(3)	-0.087(3)	-0.029(3)
O6	0.152(6)	0.057(3)	0.097(4)	0.002(3)	0.052(3)	0.055(3)
C10	0.036(3)	0.029(2)	0.050(3)	0.007(2)	0.002(3)	-0.002(3)

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The Temperature Factor has the Form of Exp(-T) Where
T = 8*(Pi**2)*U*(Sin(Theta)/Lambda)**2 for Isotropic Atoms
T = 2*(Pi**2)*Sumij(h(i)*h(j)*U(i,j)*Astar(i)*Astar(j)), for Anisotropic Atoms. Astar(i) are Reciprocal Axial Lengths and h(i) are the Reflection Indices.

Cr	-C1	2.011(4)	C12	-C13	1.394(8)
Cr	-C2	1.998(4)	C13	-C14	1.412(6)
Cr	-C3	2.005(4)	C14	-C15	1.426(6)
Cr	-C4	1.998(4)	C15	-C16	1.522(6)
Cr	-C11	2.235(5)	C16	-C19	1.538(7)
Cr	-C12	2.223(5)	C16	-C17	1.526(7)
Cr	-C13	2.164(4)	C16	-C18	1.530(7)
Cr	-C14	2.151(5)			
Cr	-C15	2.241(4)	C5	-H51	0.98
S1	-C9	1.825(4)	C5	-H53	0.98
S1	-O1	1.438(4)	C5	-H52	0.98
S1	-O2	1.437(2)	C6	-H61	0.98
S1	-O3	1.431(4)	C6	-H63	0.98
S2	-C10	1.805(5)	C6	-H62	0.98
S2	-O5	1.390(6)	C7	-H72	0.98
S2	-O4	1.418(4)	C7	-H73	0.98
S2	-O6	1.402(5)	C7	-H71	0.98
F1	-C9	1.345(5)	C8	-H81	0.98
F2	-C9	1.338(4)	C8	-H82	0.98
F3	-C9	1.331(5)	C8	-H83	0.98
F4	-C10	1.311(6)	C11	-H111	0.95
F5	-C10	1.305(6)	C12	-H121	0.95
F6	-C10	1.264(7)	C13	-H131	0.95
N1	-C5	1.444(6)	C14	-H141	0.95
N1	-C1	1.138(6)	C17	-H171	0.98
N2	-C2	1.147(6)	C17	-H172	0.98
N2	-C6	1.440(6)	C17	-H173	0.98
N3	-C7	1.435(6)	C18	-H181	0.98
N3	-C3	1.140(6)	C18	-H182	0.98
N4	-C4	1.139(6)	C18	-H183	0.98
N4	-C8	1.452(7)	C19	-H193	0.98
C11	-C15	1.415(7)	C19	-H191	0.98
C11	-C12	1.393(6)	C19	-H192	0.98

C1	-Cr	-C2	81.41(18)
C1	-Cr	-C3	129.21(19)
C1	-Cr	-C4	78.21(18)
C1	-Cr	-C11	120.67(17)
C1	-Cr	-C12	151.43(18)
C1	-Cr	-C13	127.4(2)
C1	-Cr	-C14	92.52(18)
C1	-Cr	-C15	89.65(17)
C2	-Cr	-C3	78.36(18)
C2	-Cr	-C4	133.16(19)
C2	-Cr	-C11	82.66(18)
C2	-Cr	-C12	105.15(19)
C2	-Cr	-C13	141.5(2)
C2	-Cr	-C14	134.65(17)
C2	-Cr	-C15	96.95(17)
C3	-Cr	-C4	82.75(18)
C3	-Cr	-C11	102.26(17)
C3	-Cr	-C12	79.21(18)
C3	-Cr	-C13	95.39(19)
C3	-Cr	-C14	133.59(18)
C3	-Cr	-C15	138.58(19)
C4	-Cr	-C11	143.58(18)
C4	-Cr	-C12	112.82(18)
C4	-Cr	-C13	82.3(2)
C4	-Cr	-C14	88.17(18)
C4	-Cr	-C15	124.40(19)
C11	-Cr	-C12	36.41(16)
C11	-Cr	-C13	61.38(18)
C11	-Cr	-C14	62.04(16)
C11	-Cr	-C15	36.87(17)
C12	-Cr	-C13	37.0(2)
C12	-Cr	-C14	62.80(18)
C12	-Cr	-C15	62.15(16)
C13	-Cr	-C14	38.21(18)
C13	-Cr	-C15	62.92(14)
C14	-Cr	-C15	37.83(16)
O1	-S1	-C9	103.2(2)
O1	-S1	-O2	114.4(2)
O1	-S1	-O3	116.1(2)
O3	-S1	-C9	102.4(2)
O2	-S1	-O3	115.2(2)
O2	-S1	-C9	102.94(15)
O5	-S2	-O6	116.8(3)
O6	-S2	-C10	102.1(2)
O4	-S2	-O5	115.2(4)
O5	-S2	-C10	103.2(3)
O4	-S2	-C10	104.3(3)
O4	-S2	-O6	112.8(3)
C1	-N1	-C5	179.5(4)
C2	-N2	-C6	177.1(4)
C3	-N3	-C7	175.5(5)
C4	-N4	-C8	177.9(5)
Cr	-C1	-N1	174.5(4)
Cr	-C2	-N2	174.9(4)
Cr	-C3	-N3	176.0(4)
Cr	-C4	-N4	175.5(4)
Cr	-C11	-C15	71.8(2)
C12	-C11	-C15	110.2(4)
Cr	-C11	-C12	71.3(3)
Cr	-C12	-C11	72.3(3)
C11	-C12	-C13	107.4(4)
Cr	-C12	-C13	69.2(3)
Cr	-C13	-C14	70.4(2)
C12	-C13	-C14	108.6(4)
Cr	-C13	-C12	73.8(3)
Cr	-C14	-C15	74.5(2)
C13	-C14	-C15	108.2(4)
Cr	-C14	-C13	71.4(2)
Cr	-C15	-C14	67.7(2)
Cr	-C15	-C16	134.2(3)
C11	-C15	-C16	125.1(4)
Cr	-C15	-C11	71.4(2)
C14	-C15	-C16	128.4(4)
C11	-C15	-C14	105.5(3)
C17	-C16	-C19	109.5(4)
C17	-C16	-C18	110.1(4)
C15	-C16	-C17	111.7(4)
C18	-C16	-C19	108.3(4)
C15	-C16	-C19	111.2(4)
C15	-C16	-C18	106.0(4)
F2	-C9	-F3	107.2(3)
S1	-C9	-F1	111.6(3)
S1	-C9	-F2	112.3(2)
S1	-C9	-F3	111.8(3)
F1	-C9	-F2	106.6(3)
F1	-C9	-F3	107.0(3)
S2	-C10	-F4	111.9(4)
S2	-C10	-F5	112.8(3)
S2	-C10	-F6	112.6(4)
F4	-C10	-F5	101.0(5)
F4	-C10	-F6	107.0(5)
F5	-C10	-F6	111.0(5)

N1	-C5	-H52	109.49	Cr	-C13	-H131	121.82
N1	-C5	-H51	109.44	C13	-C14	-H141	125.87
H51	-C5	-H53	109.39	Cr	-C14	-H141	119.95
H52	-C5	-H53	109.55	C15	-C14	-H141	125.89
N1	-C5	-H53	109.50	C16	-C17	-H172	109.49
H51	-C5	-H52	109.46	H172	-C17	-H173	109.41
H61	-C6	-H63	109.40	H171	-C17	-H173	109.52
H62	-C6	-H63	109.53	C16	-C17	-H171	109.49
H61	-C6	-H62	109.54	C16	-C17	-H173	109.44
N2	-C6	-H61	109.42	H171	-C17	-H172	109.49
N2	-C6	-H62	109.48	H182	-C18	-H183	109.51
N2	-C6	-H63	109.46	H181	-C18	-H182	109.47
N3	-C7	-H73	109.50	H181	-C18	-H183	109.38
H71	-C7	-H72	109.42	C16	-C18	-H181	109.41
H71	-C7	-H73	109.46	C16	-C18	-H182	109.53
N3	-C7	-H71	109.47	C16	-C18	-H183	109.52
N3	-C7	-H72	109.50	H191	-C19	-H193	109.53
H72	-C7	-H73	109.49	H192	-C19	-H193	109.46
H81	-C8	-H82	109.39	C16	-C19	-H191	109.51
H81	-C8	-H83	109.52	C16	-C19	-H192	109.45
N4	-C8	-H81	109.44	C16	-C19	-H193	109.44
N4	-C8	-H82	109.42	H191	-C19	-H192	109.44
H82	-C8	-H83	109.47				
N4	-C8	-H83	109.59				
C15	-C11	-H111	124.95				
C12	-C11	-H111	124.81				
Cr	-C11	-H111	123.62				
C13	-C12	-H121	126.35				
C11	-C12	-H121	126.25				
Cr	-C12	-H121	123.81				
C12	-C13	-H131	125.67				
C14	-C13	-H131	125.73				