Table S1. Crystal data and structure refinement for bak01.

Identification code	bak01	
Empirical formula	$C_{20}H_{41}F_6N_5O_9RhS_2$	
Formula weight	776.61	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 9.4257(5) Å	$\alpha = 72.842(1)^0$
	b = 13.4119(7) Å	$\beta = 82.082(1)^0$
	c = 13.6140(7) Å	$\gamma = 75.414(1)^0$
Volume	1587.69(14) $Å^3$	
Z	2	
Density (calculated)	1.624 Mg/m^3	
Absorption coefficient	0.757 mm^{-1}	
F(000)	798	
Crystal size	0.48 x 0.34 x 0.21 mm^3	
Crystal color, habit	yellow block	
Theta range for data collection	1.57 to 26.37^0.	
Index ranges	-11<=h<=11, -15<=k<=16,	
	0<=l<=17	
Reflections collected	18713	
Independent reflections	6457 [R(int) = 0.027]	
Completeness to theta = 26.37^0	99.7 %	
Absorption correction	Empirical with SADABS	
Max. and min. transmission	0.8572 and 0.7127	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6457 / 66 / 425	
Goodness-of-fit on F^2	1.071	
Final R indices [I>2sigma(I)]	R1 = 0.0549, wR2 = 0.1560	
R indices (all data)	R1 = 0.0641, wR2 = 0.1639	
Largest diff. peak and hole	1.324 and -1.629 e.Å-3	

[a]Quantity minimized = $R(wF^2) = \Sigma[w(F_o^2-F_c^2)]/\Sigma[(wF_o^2)^2]^{1/2}$; $R = \Sigma\Delta/\Sigma(F_o)$, $\Delta = |(F_o-F_c)|$

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for bak01. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Rh	304(1)	7561(1)	1690(1)	27(1)
S(1)	-2278(2)	7151(2)	-1638(1)	82(1)
S(2)	2804(1)	7204(1)	5085(1)	49(1)
F(1)	-2422(7)	8755(6)	-3245(4)	85(2)
F(2)	-4507(7)	8297(6)	-2783(5)	102(2)
F(3)	-3643(8)	9029(6)	-1848(5)	107(2)
F(1')	-2496(18)	8990(12)	-3093(12)	143(12)
F(2')	-3490(20)	7661(15)	-2942(16)	161(9)
F(3')	-4588(11)	8918(13)	-2228(17)	166(10)
F(4)	2000(30)	9213(12)	4713(15)	153(11)
F(5)	3223(16)	8626(14)	6017(17)	107(6)
F(6)	1150(20)	8430(20)	6190(17)	141(10)
F(4')	1530(20)	9220(13)	4882(14)	110(7)
F(5')	3580(13)	8490(20)	5710(30)	161(11)
F(6')	1410(30)	8200(20)	6360(13)	177(15)
O(1)	-1152(4)	8707(3)	797(3)	43(1)
O(2)	-649(5)	9106(3)	-144(3)	65(1)
O(3)	-3236(18)	6911(17)	-737(10)	65(6)
O(4)	-1420(20)	7745(16)	-1349(16)	92(6)
O(5)	-861(11)	6576(14)	-1915(15)	90(5)
O(3')	-3291(7)	6712(6)	-853(5)	54(2)
O(4')	-839(7)	7185(9)	-1459(8)	108(3)
O(5')	-2075(12)	6516(7)	-2344(7)	113(3)
O(6)	1479(4)	7138(4)	4753(3)	64(1)
O(7)	3322(8)	6384(4)	5970(4)	112(2)
O(8)	3859(6)	7451(7)	4257(4)	125(3)
O(9)	-119(5)	4456(4)	3552(4)	76(1)
N(1)	1015(4)	6957(3)	424(3)	37(1)
N(2)	-1115(4)	6535(3)	2039(3)	35(1)
N(3)	-457(4)	8223(3)	2935(3)	33(1)
N(4)	1693(4)	8604(3)	1314(3)	33(1)
N(5)	1706(4)	6381(3)	2658(3)	32(1)
C(1)	456(6)	5965(4)	633(4)	47(1)
C(2)	-1108(6)	6185(4)	1097(4)	45(1)
C(3)	-2623(5)	7002(4)	2440(4)	39(1)
C(4)	-2462(5)	7251(4)	3448(4)	42(1)
C(5)	-2027(5)	8290(4)	3386(4)	42(1)
C(6)	73(6)	9229(4)	2668(4)	43(1)
C(7)	1664(6)	9008(4)	2223(4)	42(1)
C(8)	3190(5)	8185(4)	869(4)	39(1)
C(9)	3040(5)	7922(4)	-111(4)	42(1)
C(10)	2591(6)	6872(4)	-44(4)	44(1)
C(11)	-3642(6)	6233(5)	2619(5)	53(1)
C(12)	-2098(7)	8380(5)	4487(5)	56(1)
C(13)	-3077(6)	9263(4)	2758(5)	53(1)
C(14)	4146(6)	8997(5)	657(5)	54(1)
C(15)	3651(6)	5908(4)	594(5)	55(1)

C(16)	2612(8)	6798(6)	-1152(5)	69(2)
C(17)	2350(6)	5690(4)	3249(4)	44(1)
C(18)	3218(7)	4783(5)	3980(5)	66(2)
C(19)	-3248(7)	8309(7)	-2413(5)	91(3)
C(20)	2301(7)	8388(5)	5524(5)	80(2)

Table S 3. Bond lengths [Å and angles [^{0}] for bak01

Rh-O(1)	2.005(3)
Rh-N(5)	2.045(4)
Rh-N(4)	2.062(4)
Rh-N(2)	2.067(4)
Rh-N(1)	2.076(4)
Rh-N(3)	2.100(4)
S(1)-O(4')	1.425(4)
S(1)-O(3')	1.425(4)
S(1)-O(5)	1.426(4)
S(1)-O(3)	1.426(4)
S(1)-O(4)	1.426(4)
S(1)-O(5')	1.427(4)
S(1)-C(19)	1.716(10)
S(1)-F(2')	2.09(2)
S(2)-O(8)	1.416(3)
S(2)-O(7)	1.417(3)
S(2)-O(6)	1.417(3)
S(2)-C(20)	1.791(7)
F(1)-C(19)	1.356(5)
F(2)-C(19)	1.356(5)
F(3)-C(19)	1.357(5)
F(1')-C(19)	1.356(5)
F(2')-C(19)	1.357(5)
F(3')-C(19)	1.356(5)
F(4)-C(20)	1.317(5)
F(5)-C(20)	1.317(5)
F(6)-C(20)	1.317(5)
F(4')-C(20)	1.317(5)
F(5')-C(20)	1.317(5)
F(6')-C(20)	1.317(5)
O(1)-O(2)	1.306(5)
N(1)-C(1)	1.490(6)
N(1)-C(10)	1.524(6)
N(2)-C(2)	1.488(6)
N(2)-C(3)	1.500(6)
N(3)-C(6)	1.483(6)
N(3)-C(5)	1.513(6)
N(4)-C(7)	1.483(6)
N(4)-C(8)	1.497(6)
N(5)-C(17)	1.133(6)
C(1)-C(2)	1.515(7)
C(3)-C(11)	1.526(7)
C(3)-C(4)	1.540(7)
C(4)-C(5)	1.525(7)
C(5)-C(12)	1.529(7)
C(5)-C(13)	1.529(7)
C(6)-C(7)	1.529(7)
C(8)-C(9)	1.510(7)
C(8)-C(14)	1.522(6)
C(9)-C(10)	1.543(6)
C(10)-C(15)	1.533(8)
C(10)-C(16)	1.538(8)

C(17)-C(18)	1.466(8)
O(1)-Rh-N(5)	177.15(13)
O(1)-Rh-N(4)	87.98(14)
N(5)-Rh-N(4)	93.89(15)
O(1)-Rh-N(2)	90.79(15)
N(5)-Rh-N(2)	87.36(15)
N(4)-Rh-N(2)	178.71(15)
O(1)-Rh-N(1)	87.34(16)
N(5)-Rh-N(1)	94.65(16)
N(4)-Rh-N(1)	94.71(15)
N(2)-Rh-N(1)	84.84(14)
O(1)-Rh-N(3)	90.62(15)
N(5)-Rh-N(3)	87.41(15)
N(4)-Rh-N(3)	84.68(15)
N(2)-Rh-N(3)	95.72(14)
N(1)-Rh-N(3)	177.89(15)
O(4')-S(1)-O(3')	123.9(6)
O(4')-S(1)-O(5)	48.4(8)
O(3')-S(1)-O(5)	125.1(9)
O(4')-S(1)-O(3)	115.3(10)
O(3')-S(1)-O(3)	14.7(9)
O(5)-S(1)-O(3)	130.6(12)
O(4')-S(1)-O(4)	34.8(8)
O(3')-S(1)-O(4)	115.6(9)
O(5)-S(1)-O(4)	82.2(12)
O(3)-S(1)-O(4)	101.6(12)
O(4')-S(1)-O(5')	105.7(6)
O(3')-S(1)-O(5')	103.6(6)
O(5)-S(1)-O(5')	58.0(9)
O(3)-S(1)-O(5')	118.3(10)
O(4)-S(1)-O(5')	135.8(10)
O(4')-S(1)-C(19)	115.1(5)
O(3')-S(1)-C(19)	107.3(4)
O(5)-S(1)-C(19)	124.9(8)
O(3)-S(1)-C(19)	104.4(9)
O(4)-S(1)-C(19)	90.4(9)
O(5')-S(1)-C(19)	96.9(5)
O(4')-S(1)-F(2')	134.2(7)
O(3')-S(1)-F(2')	101.9(7)
O(5)-S(1)-F(2')	107.0(10)
O(3)-S(1)-F(2')	109.3(10)
O(4)-S(1)-F(2')	126.2(10)
O(5')-S(1)-F(2')	58.9(6)
C(19)-S(1)-F(2')	40.3(4)
O(8)-S(2)-O(7)	116.6(5)
O(8)-S(2)-O(6)	112.6(4)
O(7)-S(2)-O(6)	114.9(4)
O(8)-S(2)-C(20)	103.1(4)
O(7)-S(2)-C(20)	103.6(3)
O(6)-S(2)-C(20)	103.9(3)
C(19)-F(2')-S(1)	54.9(9)
O(2)-O(1)-Rh	115.3(3)
C(1)-N(1)-C(10)	114.8(4)

C(1)-N(1)-Rh	106.5(3)
C(10)-N(1)-Rh	121.7(3)
C(2)-N(2)-C(3)	113.6(4)
C(2)-N(2)-Rh	106.5(3)
C(3)-N(2)-Rh	113.8(3)
C(6)-N(3)-C(5)	115.9(4)
C(6)-N(3)-Rh	105.3(3)
C(5)-N(3)-Rh	120.9(3)
C(7)-N(4)-C(8)	115.5(4)
C(7)-N(4)-Rh	107.3(3)
C(8)-N(4)-Rh	115.1(3)
C(17)-N(5)-Rh	172.5(4)
N(1)-C(1)-C(2)	107.8(4)
N(2)-C(2)-C(1)	108.7(4)
N(2)-C(3)-C(11)	111.2(4)
N(2)-C(3)-C(4)	107.6(4)
C(11)-C(3)-C(4)	111.1(4)
C(5)-C(4)-C(3)	118.9(4)
N(3)-C(5)-C(4)	108.8(4)
N(3)-C(5)-C(12)	108.5(4)
C(4)-C(5)-C(12)	107.6(4)
N(3)-C(5)-C(13)	111.6(4)
C(4)-C(5)-C(13)	111.4(4)
C(12)-C(5)-C(13)	108.9(4)
N(3)-C(6)-C(7)	108.4(4)
N(4)-C(7)-C(6)	107.8(4)
N(4)-C(8)-C(9)	109.1(4)
N(4)-C(8)-C(14)	111.0(4)
C(9)-C(8)-C(14)	110.5(4)
C(8)-C(9)-C(10)	119.4(4)
N(1)-C(10)-C(15)	111.9(4)
N(1)-C(10)-C(16)	107.9(4)
C(15)-C(10)-C(16)	111.1(5)
N(1)-C(10)-C(9)	107.9(4)
C(15)-C(10)-C(9)	110.5(4)
C(16)-C(10)-C(9)	107.4(5)
N(5)-C(17)-C(18)	177.8(6)
F(1)-C(19)-F(2)	105.7(5)
F(1)-C(19)-F(3')	116.3(12)
F(2)-C(19)-F(3')	55.5(9)
F(1)-C(19)-F(1')	17.5(9)
F(2)-C(19)-F(1')	112.2(12)
F(3')-C(19)-F(1')	105.6(5)
F(1)-C(19)-F(3)	105.7(5)
F(2)-C(19)-F(3)	105.6(5)
F(3')-C(19)-F(3)	50.1(9)
F(1')-C(19)-F(3)	88.2(9)
F(1)-C(19)-F(2')	88.9(9)
F(2)-C(19)-F(2')	50.4(8)
F(3')-C(19)-F(2')	105.6(5)
F(1')-C(19)-F(2')	105.6(5)
F(3)-C(19)-F(2')	155.3(9)
F(1)-C(19)-S(1)	112.8(6)
F(2)-C(19)-S(1)	119.3(6)

F(3')-C(19)-S(1)	129.8(9)
F(1')-C(19)-S(1)	118.7(9)
F(3)-C(19)-S(1)	106.7(6)
F(2')-C(19)-S(1)	84.9(11)
F(5)-C(20)-F(6')	91.7(17)
F(5)-C(20)-F(6)	99.6(15)
F(6')-C(20)-F(6)	17(2)
F(5)-C(20)-F(5')	23.6(16)
F(6')-C(20)-F(5')	112.8(19)
F(6)-C(20)-F(5')	122.7(17)
F(5)-C(20)-F(4')	114.2(14)
F(6')-C(20)-F(4')	104.3(17)
F(6)-C(20)-F(4')	87.6(16)
F(5')-C(20)-F(4')	115.9(19)
F(5)-C(20)-F(4)	105.3(16)
F(6')-C(20)-F(4)	124(2)
F(6)-C(20)-F(4)	107.8(18)
F(5')-C(20)-F(4)	100(2)
F(4')-C(20)-F(4)	21(2)
F(5)-C(20)-S(2)	120.7(9)
F(6')-C(20)-S(2)	107.6(13)
F(6)-C(20)-S(2)	114.9(11)
F(5')-C(20)-S(2)	102.3(10)
F(4')-C(20)-S(2)	113.9(12)
F(4)-C(20)-S(2)	107.6(11)

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for bak01. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Rh	25(1)	22(1)	34(1)	-6(1)	1(1)	-6(1)
S(1)	52(1)	96(1)	62(1)	15(1)	7(1)	-3(1)
S(2)	38(1)	46(1)	62(1)	-17(1)	-1(1)	-6(1)
F(4)	310(30)	34(8)	119(12)	11(8)	-84(16)	-42(12)
F(5)	135(11)	65(7)	151(14)	-63(9)	-79(10)	1(7)
F(6)	135(14)	121(12)	180(20)	-104(15)	-10(14)	29(11)
F(4')	103(8)	71(10)	165(17)	-61(10)	-73(9)	32(7)
F(5')	155(15)	156(17)	240(20)	-148(15)	-66(15)	-8(12)
F(6')	200(20)	250(30)	57(7)	-83(11)	-12(10)	57(19)
O(1)	32(2)	39(2)	57(2)	-14(2)	-1(2)	-6(1)
O(2)	65(3)	49(2)	64(3)	11(2)	-11(2)	-12(2)
O(6)	56(2)	75(3)	67(3)	-23(2)	-10(2)	-18(2)
O(7)	135(5)	50(3)	140(5)	-1(3)	-80(5)	6(3)
O(8)	69(4)	201(8)	130(5)	-86(6)	52(4)	-60(4)
O(9)	66(3)	54(3)	96(4)	-5(3)	16(3)	-21(2)
N(1)	35(2)	36(2)	42(2)	-15(2)	9(2)	-16(2)
N(2)	31(2)	32(2)	43(2)	-13(2)	5(2)	-11(2)
N(3)	31(2)	30(2)	38(2)	-10(2)	-4(2)	-4(2)
N(4)	33(2)	25(2)	41(2)	-5(2)	-2(2)	-9(1)
N(5)	26(2)	26(2)	42(2)	-6(2)	1(2)	-6(1)
C(1)	49(3)	47(3)	55(3)	-27(2)	14(2)	-24(2)
C(2)	44(3)	52(3)	52(3)	-24(2)	8(2)	-26(2)
C(3)	24(2)	42(3)	51(3)	-11(2)	4(2)	-10(2)
C(4)	28(2)	47(3)	46(3)	-13(2)	9(2)	-5(2)
C(5)	31(2)	44(3)	47(3)	-18(2)	5(2)	0(2)
C(6)	50(3)	30(2)	52(3)	-17(2)	-6(2)	-7(2)
C(7)	47(3)	37(2)	49(3)	-12(2)	-4(2)	-20(2)
C(8)	31(2)	31(2)	54(3)	-6(2)	2(2)	-12(2)
C(9)	38(2)	37(2)	50(3)	-10(2)	12(2)	-18(2)
C(10)	41(3)	44(3)	53(3)	-23(2)	19(2)	-20(2)
C(11)	35(3)	58(3)	71(4)	-21(3)	7(2)	-22(2)
C(12)	54(3)	63(4)	53(3)	-29(3)	10(3)	-11(3)
C(13)	42(3)	45(3)	66(4)	-21(3)	0(3)	2(2)
C(14)	41(3)	44(3)	81(4)	-16(3)	5(3)	-21(2)
C(15)	40(3)	42(3)	82(4)	-27(3)	19(3)	-11(2)
C(16)	73(4)	94(5)	61(4)	-44(4)	31(3)	-45(4)
C(17)	36(2)	37(3)	56(3)	-10(2)	-1(2)	-6(2)
C(18)	68(4)	41(3)	76(4)	4(3)	-19(3)	-6(3)
C(19)	113(7)	97(6)	76(5)	-17(5)	6(5)	-58(6)
C(20)	98(6)	68(5)	83(5)	-34(4)	-40(5)	-1(4)

Table S5. Hydrogen coordinates (x 104) and isotropic displacement parameters ($Å^2$x 10^3) for bak01.

	x	y	z	U(eq)
H(9C)	-130(80)	4260(60)	2900(30)	91
H(9D)	-750(70)	4160(60)	4170(30)	91
H(1)	457	7441	-100	44
H(2)	-716	5934	2551	42
H(3)	105	7769	3470	40
H(4)	1258	9190	801	40
H(1A)	1077	5366	1118	56
H(1B)	482	5766	-15	56
H(2A)	-1740	6752	593	54
H(2B)	-1498	5529	1277	54
H(3A)	-3042	7684	1925	47
H(4A)	-3411	7250	3862	50
H(4B)	-1723	6652	3836	50
H(6A)	15	9478	3291	51
H(6B)	-548	9793	2155	51
H(7A)	2036	9673	2015	50
H(7B)	2294	8467	2745	50
H(8)	3666	7515	1375	47
H(9A)	3994	7914	-520	50
H(9B)	2309	8520	-509	50
H(11A)	-3698	6068	1973	79
H(11B)	-4625	6567	2860	79
H(11C)	-3256	5571	3140	79
H(12A)	-1557	7708	4923	84
H(12B)	-3126	8522	4757	84
H(12C)	-1655	8968	4486	84
H(13A)	-2839	9920	2799	79
H(13B)	-4090	9249	3036	79
H(13C)	-2974	9245	2038	79
H(14A)	3715	9645	136	81
H(14B)	5135	8689	403	81
H(14C)	4204	9179	1294	81
H(15A)	3491	5906	1321	82
H(15B)	4666	5956	350	82
H(15C)	3473	5246	518	82
H(16A)	2404	6113	-1135	104
H(16B)	3582	6848	-1503	104
H(16C)	1862	7387	-1524	104
H(18A)	3928	4334	3602	99
H(18B)	2562	4357	4441	99
H(18C)	3742	5049	4387	99

Figure Captions

Figure S-1. UV-visible spectra of (a) $Cr_{aq}OO^{2+}$ and (b) L^2RhOO^{2+} in 0.1 M $HClO_4$.

Figure S-2. Spectrum of 0.10 mM L^2RhH^{2+} (a) before and (b) after the reaction with 0.012 mM $Cr_{aq}O^{2+}$ in O_2-saturated 0.1 M $HClO_4$. The absorbing species in (b) are L^2RhOO^{2+} and the unreacted L^2RhH^{2+}.

Figure S-3. Visible spectrum of $(salen)CrO^+$ in aqueous solution.

Figure S-4. An ORTEP of the crystallographic asymmetric unit of $[L^2(CH_3CN)RhOO](CF_3SO_3)_2.H_2O$

Figure S-5. Hydrogen bonding network in the lattice of $[L^2(CH_3CN)RhOO](CF_3SO_3)_2.H_2O$

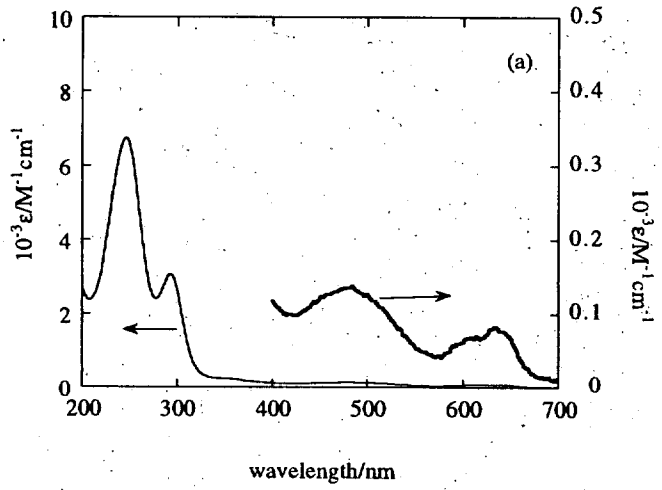

Figure S-1a

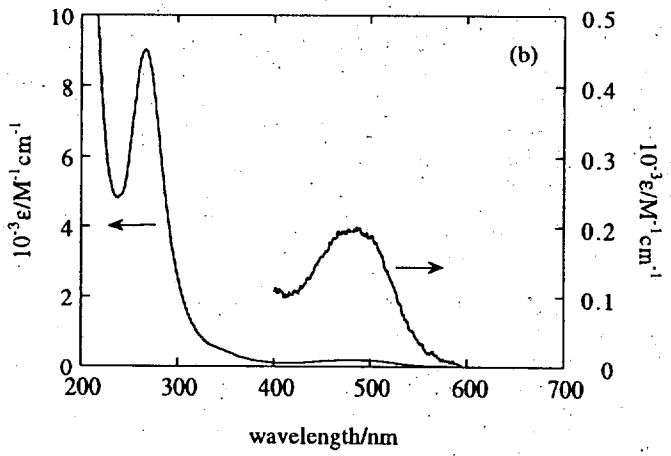

Figure S-1b

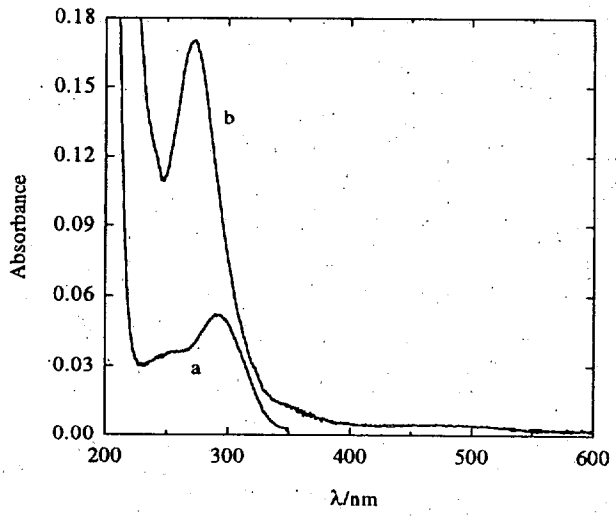
0.18
0.15
0.12
0.09
0.06
0.03
0.00
Absorbance
b
a
200
300
400
500
600
λ/nm

Figure S-2

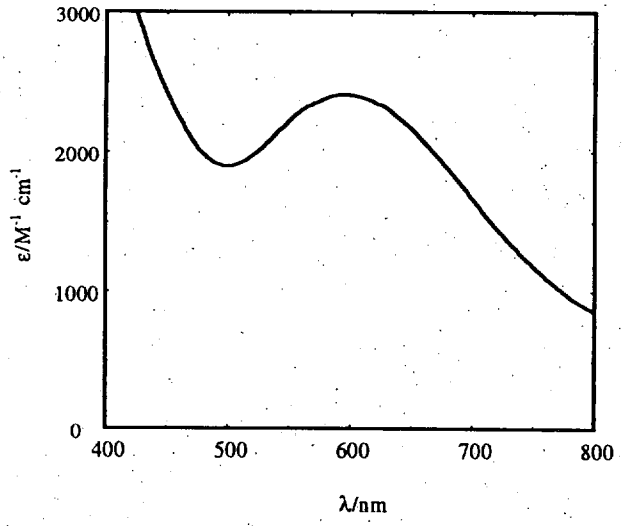

Figure S-3

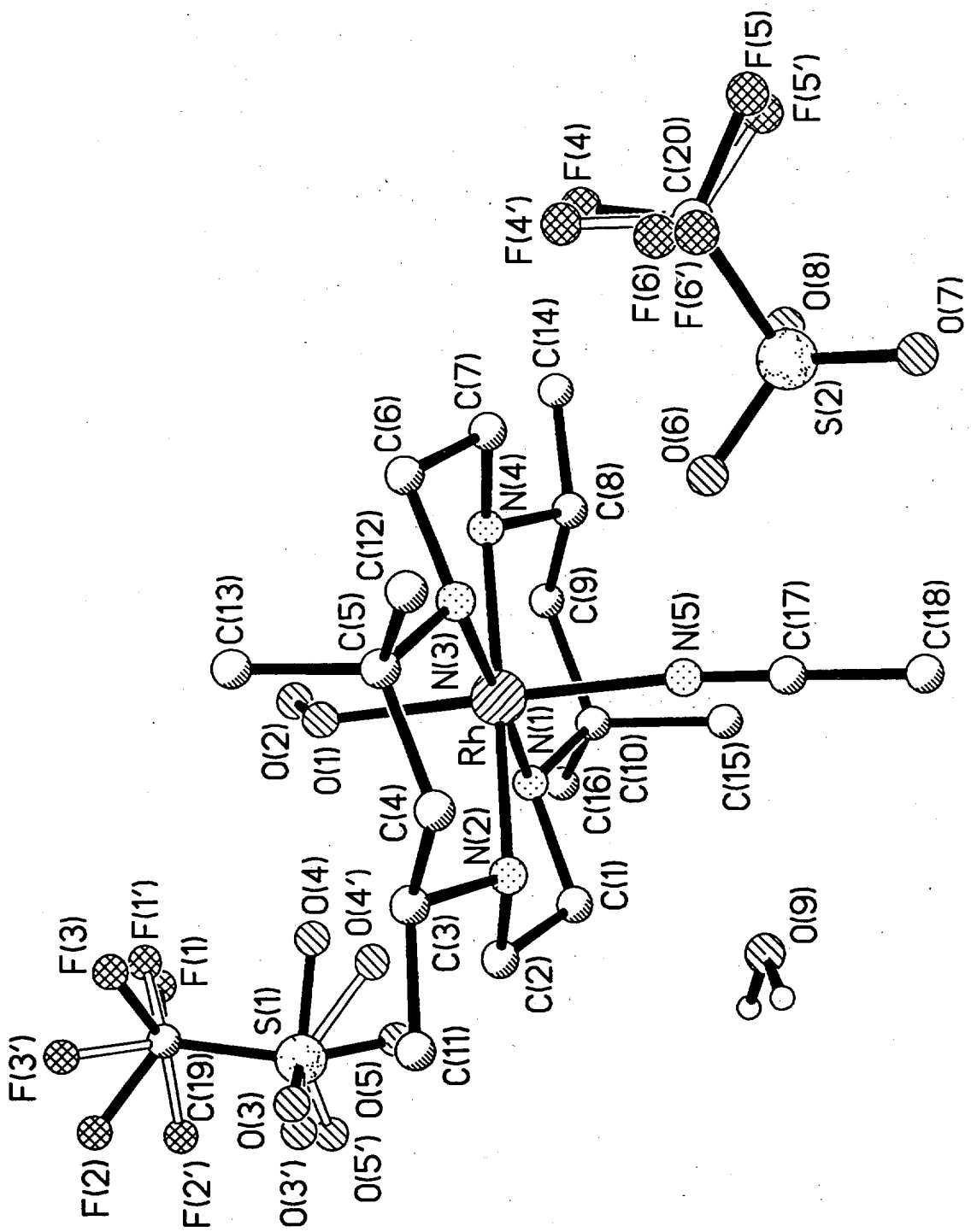
F(5)
F(5')
F(4)
F(4')
C(20)
F(6)
F(6')
O(8)
O(7)
O(6)
S(2)
C(14)
C(7)
C(6)
N(4)
C(8)
C(12)
C(5)
C(9)
C(13)
N(3)
N(5)
C(17)
C(18)
O(2)
O(1)
Rh
N(1)
C(16)
C(10)
C(15)
C(4)
N(2)
C(1)
O(4)
O(4')
F(3)
F(1')
F(1)
C(3)
C(2)
O(9)
S(1)
F(3')
C(19)
C(11)
O(3)
O(5)
F(2)
F(2')
O(3')
O(5')

Fig S4

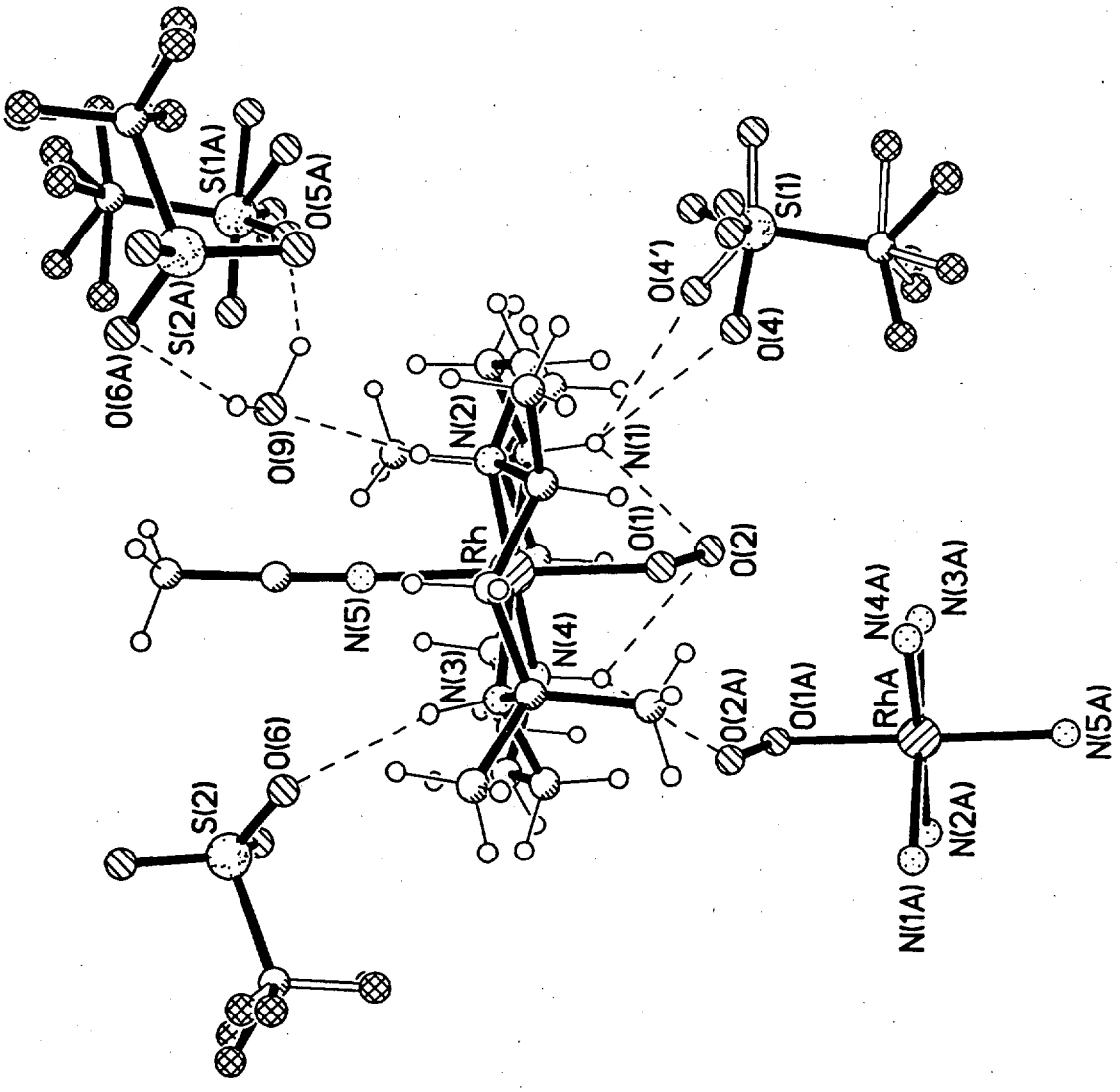
O(6A)
S(2A)
S(1A)
O(5A)
O(9)
N(2)
N(1)
O(4')
S(1)
O(4)
Rh
O(1)
O(2')
N(5)
N(4)
N(3)
O(6)
S(2)
O(2A)
O(1A)
RhA
N(4A)
N(3A)
N(5A)
N(2A)
N(1A)

Fig S5