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"A Bis(pyrazolyl) (bipyridyl) Platinum Complex"

by

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A Bis(pyrazolyl) (bipyridyl) Platinum Complex

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(Received ; Accepted)

Abstract. Bis(3,5-dimethylpyrazolium)4,4'-dimethyl-2,2'-bipyridyl platinum(II)·0.5 tetrahydrofuran solvate·H₂O, PtC₂₄H₃₂N₆O_{1.5}, M_r = 623.65; monoclinic, $P2_1/n$; $a = 8.625(2)$, $b = 20.593(8)$, $c = 14.451(4)$ Å, $\beta = 90.32(2)^\circ$, $V = 2566.7(14)$ Å³, $Z = 4$, $D_x = 1.61$ g cm⁻³, MoK α , 0.71073 Å, $\mu = 55.50$ cm⁻¹, $F(000) = 1232$, room temperature, $R = 0.0387$ for 2874 reflections with $F_o^2 > 3\sigma(F_o^2)$. The square-planar Pt complex has normal Pt-N(bipyridyl) bonds (2.009(8) Å) and slightly short Pt-N(pyrazolyl) bonds (1.983(7) Å). The ligand molecules have normal distances and angles; the planes of the pyrazolyl ligands are twisted by about 60° to the bipyridyl-Pt plane, with the closest contacts between the pyrazolyls being ~ 3.3 Å (C14...N5 and C19...N3).

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Introduction. In the course of our work on platinum(II) pyrazolyl bridged dimers, we have prepared a series of bis(pyrazolyl)bipyridyl platinum(II) monomers. These complexes have emissive states of MLCT or π - π^* character, depending on the substituents on the pyrazole ring. Here we report the structure of bis(3,5-dimethylpyrazolium)-4,4'-dimethyl-2,2'-bipyridyl platinum(II), a derivative synthesized according to the literature method for the unmethylated analogue (Minghetti et al., 1979).

Experimental. Crystal a yellow needle, $0.07 \times 0.07 \times 0.36$ mm; CAD-4 diffractometer, ω scans; 25 reflections with $14^\circ < 2\theta < 16^\circ$ used for unit cell; absorption correction based on ψ scans of 6 reflections, relative transmissions from 0.882 to 1.000; $(\sin\theta/\lambda)_{\max}$, $0.59 \text{ \AA}^{-1}$; h from -10 to 10 , k from -24 to 24 , l from 0 to 17 ; three standard reflections (204 , $2\bar{5}2$, $2\bar{3}3$) showed no variations greater than predicted by counting statistics; 9834 reflections measured, 4501 independent; goodness of fit for merging 4368 multiples, 0.974; $R_{\text{merge}} = 0.041$ for 3377 duplicates. All reflections used in solution and refinement of the structure; Pt atom located from Patterson map, remaining heavy atoms found by successive structure factor-Fourier calculations; F^2 values used in least squares, with $w = 1/\sigma^2(F_o^2)$; hydrogen atoms positioned by calculation ($\text{C-H} = 0.95 \text{ \AA}$) and not refined; coordinates and anisotropic displacement parameters of all atoms in the Pt molecule and the water O atom plus a scale factor refined; R (on F) for 3933 reflections with $F_o^2 > 0$, 0.062; wR (on F^2), 0.0078; $S = 1.49$ for 271 parameters and 4501 reflections; weights taken as $1/\sigma^2(F_o^2)$; variances ($\sigma^2(F_o^2)$) derived from counting statistics plus an additional term, $(0.014I)^2$; variances of the merged data by propagation of error plus another additional term, $(0.014\bar{I})^2$. $(\Delta/\sigma)_{\max}$, 0.01; final difference map has 1 peak $2.2 \text{ e\AA}^{-3}$, $1.8 \text{ \AA}$ from C18 and C19, next highest $1.4 \text{ e\AA}^{-3}$ near the Pt atom; largest negative peak, $-1.9 \text{ e\AA}^{-3}$, near C23 of disordered THF. Atomic scattering factors and dispersion corrections from Cromer and Waber (1974) and Cromer (1974); computer programs were those of the CRYM Crystallographic Computing System (Duchamp, 1964) and ORTEP (Johnson, 1976). Final

refined parameters of the atoms are listed in Table 1. * The tetrahydrofuran molecule is located near a center of symmetry and its parameters could not be refined; an idealized THF molecule was positioned based on difference maps.

We collected data for this compound with a crystal that had $\beta = 90.14^\circ$, solved and refined the structure, but large peaks in the difference map and distorted geometry in pyrazolyl ligand 2 caused us to conclude that our crystal was bad. The results reported here are based on data from a crystal that showed no sign of any twinning or deformity; still, the large positive peak in the difference map is near where the worst one was for the first crystal.

Discussion.

A drawing of the molecule including the numbering system is shown in Figure 1, and Table 2 gives distances and angles in the molecule. The packing is shown in Figure 2. The Pt-N distances to the bipyridyl N atoms are equal at 2.009(13) Å, and to the pyrazolyl N atoms at 1.983(11) Å. Distances and angles in the ligand atoms are normal, with C-CH₃ bonds being a bit short, especially in the pyrazolyl ligands (C18-C19, 1.449(14) Å is the shortest). The pyrazolyl ligands are twisted out of the Pt-bipyridyl plane by 64(3)° each. This orientation is comparable to other cis-bis nitrogen heterocycle platinum(II) systems (41.7° for cis-[Pt(N-methylimidazole)₂Cl₂] (Graves, Hodgson, van Kralingen & Reedijk, 1978) and 55.3° and 73.2° for cis-[Pt(pyrazole)₂Cl₂] (Cinellu *et al.*, 1989). There are short distances between N3 and C19 (3.32(1) Å) and N5 and C14 (3.33(1) Å). The hydrogen atoms on C14 and C19 show up as two sets of three H atoms each in the plane where they are expected, but none of them points toward the close nitrogen atom. The water

* Lists of assigned hydrogen parameters, anisotropic displacement parameters, complete distances and angles, and observed and calculated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP XXXXX (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, ENGLAND.

molecule is 2.82(1) Å from N4, indicating a hydrogen bond between them; there are also contacts between the water molecule and C5 and C8 in a different molecule (3.30(1) and 3.20(1) Å). The Pt-O(water) distance (4.492(7) Å) and all other intermolecular distances are at van der Waals' distances or greater.

Acknowledgment. This research was supported by the Office of Naval Research.

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Legends to Figures

Figure 1. An ORTEP drawing of the molecule showing the numbering system. Heavy atoms are shown as 50% probability ellipsoids, hydrogen atoms as spheres of small, arbitrary size.

Figure 2. An ORTEP projection down the *a* axis, with 50% probability ellipsoids. The contents of one unit cell (not including hydrogen atoms) are shown, plus three additional THF molecules. Only one molecular orientation is shown at each THF site.

Supplementary Material for:

A Bis(pyrazolyl) (bipyridyl) Platinum Complex

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Abstract. $\text{Pt}(\text{3,5-dimethylpyrazolium})_2(4,4'\text{-dimethyl-2,2'-bipyridyl})\text{Pt}(\text{II}) \cdot 0.5$ tetrahydrofuran solvate $\cdot \text{H}_2\text{O}$, $\text{PtC}_{24}\text{H}_{32}\text{N}_6\text{O}_{1.5}$, $M_r = 623.65$; monoclinic, $P2_1/n$; $a = 8.625(2)$, $b = 20.593(8)$, $c = 14.451(4)$ Å, $\beta = 90.32(2)^\circ$, $V = 2566.7(14)$ Å³, $Z = 4$, $D_z = 1.61$ g cm⁻³, MoK α , 0.71073 Å, $\mu = 55.50$ cm⁻¹, $F(000) = 1232$, room temperature, $R = 0.0387$ for 2874 reflections with $F_o^2 > 3\sigma(F_o^2)$. The square-planar Pt complex has normal Pt-N(bipyridyl) bonds (2.009(8) Å) and slightly short Pt-N(pyrazolyl) bonds (1.983(7) Å). The ligand molecules have normal distances and angles; the planes of the pyrazolyl ligands are twisted by about 60° to the bipyridyl-Pt plane, with the closest contacts between the pyrazolyls being ~ 3.3 Å (C14...N5 and C19...N3).

* Contribution No. 8555

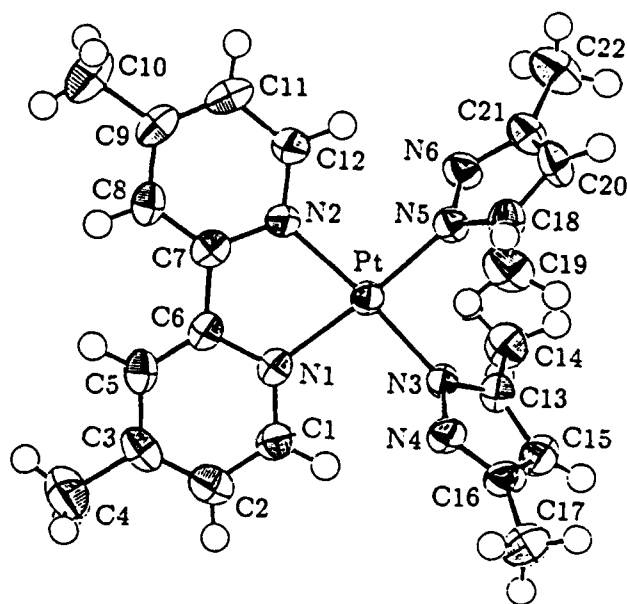


Figure 1. Schaefer, Connick, Mukowski
& Gray

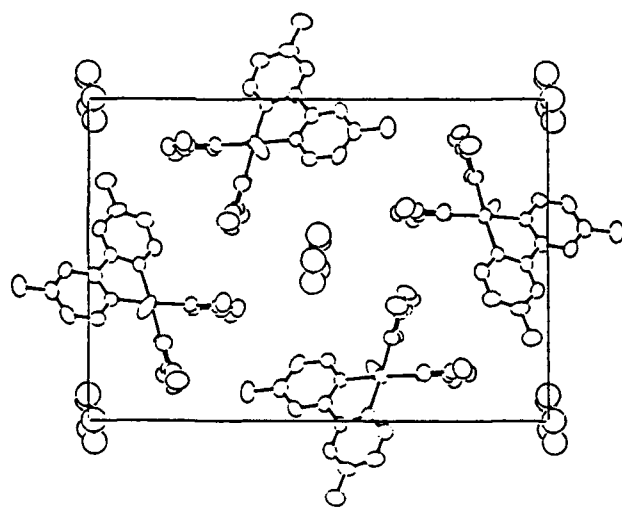


Figure 2. Schaefer, Connick, Miskowski
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Table 1. Final Refined Parameters for
Bis(3,5-dimethylpyrazolium)(5,5'-dimethyl-2,2'-dipyridyl) Platinum(II).

x, y, z and $U_{eq}^a \times 10^4$				
Atom	x	y	z	U_{eq}
Pt	2451(.4)	1366(.2)	3618(.3)	372(1)
N1	1470(8)	1091(3)	4821(5)	396(18)
C1	540(10)	1446(5)	5346(7)	491(24)
C2	-19(11)	1231(5)	6192(7)	579(29)
C3	380(11)	620(5)	6506(7)	519(29)
C4	-198(14)	363(6)	7413(8)	818(38)
C5	1326(11)	243(4)	5948(7)	486(25)
C6	1867(9)	480(4)	5124(7)	393(22)
C7	2904(9)	129(4)	4492(7)	412(24)
C8	3346(11)	-506(4)	4646(7)	495(25)
C9	4327(11)	-804(5)	4013(8)	537(27)
C10	4760(14)	-1510(5)	4131(9)	810(39)
C11	4858(11)	-452(5)	3263(8)	539(27)
C12	4342(11)	194(5)	3147(7)	488(25)
N2	3379(8)	481(3)	3747(5)	384(18)
N3	1428(8)	2224(3)	3584(5)	396(19)
C13	2057(10)	2817(4)	3578(7)	445(24)
C14	3747(11)	2936(5)	3683(8)	615(29)
C15	872(12)	3267(5)	3496(7)	567(28)
C16	-471(10)	2901(5)	3445(7)	501(26)

Table 1. (Cont.)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
C17	−2140(12)	3126(5)	3354(8)	735(34)
N4	−161(8)	2272(4)	3502(5)	454(21)
N5	3488(8)	1581(3)	2430(5)	413(19)
C18	2854(11)	1740(5)	1615(7)	487(26)
C19	1160(12)	1696(6)	1420(8)	709(34)
C20	4045(12)	1901(5)	1020(7)	589(30)
C21	5428(11)	1837(5)	1529(7)	498(26)
C22	7058(12)	1937(6)	1233(8)	805(38)
N6	5087(8)	1639(4)	2389(6)	489(21)
W1	7648(8)	1255(3)	3509(6)	901(23)

$$^a U_{eq} = \frac{1}{3} \sum_i \sum_j [U_{ij}(a_i^* a_j^*)(\vec{a}_i \cdot \vec{a}_j)]$$

Table 2. Distances and Angles not Involving Hydrogen in
Bis(3,5-dimethylpyrazolium)(5,5'-dimethyl-2,2'-dipyridyl) Platinum(II).

Distance(Å)			Distance(Å)		
Pt	-N1	2.018(7)	N3	-N4	1.379(10)
Pt	-N2	2.000(7)	C13	-C14	1.485(13)
Pt	-N3	1.975(7)	C13	-C15	1.384(13)
Pt	-N5	1.990(7)	C15	-C16	1.383(14)
N1	-C1	1.327(12)	C16	-C17	1.517(15)
N1	-C6	1.376(11)	C16	-N4	1.326(12)
C1	-C2	1.389(14)	N5	-C18	1.338(12)
C2	-C3	1.381(14)	N5	-N6	1.386(10)
C3	-C4	1.501(15)	C18	-C19	1.489(14)
C3	-C5	1.388(14)	C18	-C20	1.383(14)
C5	-C6	1.371(13)	C20	-C21	1.404(14)
C6	-C7	1.471(12)	C21	-C22	1.486(15)
C7	-C8	1.379(13)	C21	-N6	1.342(12)
C7	-N2	1.363(11)			
C8	-C9	1.391(14)			
C9	-C10	1.512(15)			
C9	-C11	1.384(14)			
C11	-C12	1.412(14)			
C12	-N2	1.341(12)			
N3	-C13	1.337(11)			

Table 2. (Cont.)

Angle(°)		Angle(°)	
N1 -Pt -N2	80.4(3)	C10 -C9 -C8	120.1(9)
N1 -Pt -N3	94.8(3)	C11 -C9 -C8	119.3(9)
N1 -Pt -N4	84.4(2)	C11 -C9 -C10	120.7(9)
N2 -Pt -N3	175.2(3)	C12 -C11 -C9	118.8(9)
N2 -Pt -N4	153.3(2)	N2 -C12 -C11	122.2(8)
N3 -Pt -N4	23.9(2)	C12 -N2 -C7	117.9(7)
C6 -N1 -C1	118.2(7)	N4 -N3 -C13	109.7(7)
C2 -C1 -N1	122.8(9)	C14 -C13 -N3	123.2(8)
C3 -C2 -C1	119.6(9)	C15 -C13 -N3	108.2(8)
C4 -C3 -C2	121.7(9)	C15 -C13 -C14	128.6(9)
C5 -C3 -C2	117.7(9)	C16 -C15 -C13	105.0(9)
C5 -C3 -C4	120.7(9)	C17 -C16 -C15	129.2(9)
C6 -C5 -C3	120.7(9)	N4 -C16 -C15	111.2(8)
C5 -C6 -N1	121.1(8)	N4 -C16 -C17	119.6(8)
C7 -C6 -N1	113.8(7)	C16 -N4 -N3	105.9(7)
C7 -C6 -C5	125.2(8)	N6 -N5 -C18	110.0(7)
C8 -C7 -C6	122.3(8)	C19 -C18 -N5	123.2(8)
N2 -C7 -C6	114.6(7)	C20 -C18 -N5	107.7(8)
N2 -C7 -C8	123.2(8)	C20 -C18 -C19	128.9(9)
C9 -C8 -C7	118.7(9)	C21 -C20 -C18	106.5(9)

Table 2. (Cont.)

Angle(°)		
C22 -C21 -C20	129.7(9)	
N6 -C21 -C20	108.9(8)	
N6 -C21 -C22	121.4(9)	
C21 -N6 -N5	106.8(7)	

Table S1. Non-Refined Parameters for
Bis(3,5-dimethylpyrazolium)(5,5'-dimethyl-2,2'-dipyridyl) Platinum(II).

x, y, z and $U_{eq}^a \times 10^4$					
Atom	x	y	z	B	
O	5040	-30	660	10.0	*
C23	4770	20	-270	10.0	*
C24	6150	130	-670	10.0	*
C25	7280	110	10	10.0	*
C26	6630	-10	800	10.0	*
H1	253	1864	5135	4.5	*
H2	-665	1504	6554	5.3	*
H4A	205	-64	7508	7.6	*
H4B	169	636	7902	7.6	*
H4C	-1287	352	7415	7.6	*
H5	1587	-183	6135	4.3	*
H8	3009	-741	5171	4.5	*
H10A	4296	-1672	4683	7.3	*
H10B	4402	-1752	3617	7.3	*
H10C	5856	-1549	4183	7.3	*
H11	5555	-644	2837	4.9	*
H12	4699	434	2627	4.5	*
H14A	4273	2526	3723	5.7	*
H14B	4120	3169	3169	5.7	*
H14C	3942	3173	4237	5.7	*
H15	969	3730	3494	5.0	*
H17A	-2794	2755	3330	6.5	*
H17B	-2405	3387	3869	6.5	*
H17C	-2259	3370	2800	6.5	*
H19A	634	1576	1960	6.5	*
H19B	802	2110	1210	6.5	*
H19C	988	1384	944	6.5	*
H20	3939	2030	394	5.2	*
H22A	7735	1860	1739	7.4	*
H22B	7292	1658	738	7.4	*
H22C	7178	2380	1036	7.4	*
H23A	4332	-372	-499	10.0	*
H23B	4083	370	-393	10.0	*
H24A	6146	545	-958	10.0	*
H24B	6348	-195	-1121	10.0	*
H25A	8006	-223	-128	10.0	*
H25B	7800	516	39	10.0	*
H26A	6882	323	1230	10.0	*
H26B	6982	-416	1032	10.0	*

Table S2. Anisotropic Displacement Parameters for
Bis(3,5-dimethylpyrazolium)(5,5'-dimethyl-2,2'-dipyridyl) Platinum(II).

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	306(2)	378(2)	432(2)	8(2)	-2(1)	44(2)
N1	381(42)	351(41)	455(49)	-27(33)	-60(37)	-15(36)
C1	441(53)	453(59)	579(66)	19(48)	33(49)	-17(54)
C2	524(61)	736(82)	477(66)	2(55)	38(51)	-34(59)
C3	394(58)	772(78)	392(63)	-150(53)	-30(49)	60(57)
C4	1039(98)	862(89)	554(79)	-144(73)	115(71)	72(67)
C5	518(61)	408(56)	531(68)	-95(47)	-58(53)	92(50)
C6	326(48)	347(51)	506(63)	-36(40)	-74(45)	14(46)
C7	260(47)	450(56)	524(65)	-30(40)	-115(45)	-33(49)
C8	531(61)	396(56)	558(68)	-64(47)	-44(53)	88(50)
C9	518(62)	422(59)	670(77)	97(50)	-172(57)	-57(57)
C10	989(90)	457(73)	980(98)	131(60)	-262(77)	-36(63)
C11	449(60)	488(62)	680(77)	131(48)	-111(55)	-179(57)
C12	529(61)	509(61)	426(62)	68(49)	52(50)	-3(49)
N2	354(42)	377(43)	421(48)	19(34)	42(37)	7(37)
N3	310(40)	409(45)	470(49)	18(33)	43(36)	83(37)
C13	477(63)	413(54)	446(59)	1(44)	-8(52)	58(48)
C14	501(62)	552(67)	792(84)	-98(51)	1(60)	41(59)
C15	585(68)	450(61)	667(77)	41(53)	21(58)	45(54)
C16	393(56)	618(68)	493(66)	153(50)	-23(49)	18(53)
C17	587(74)	768(78)	851(93)	207(59)	-25(63)	83(67)
N4	260(40)	491(49)	610(56)	34(35)	-29(38)	26(41)
N5	316(40)	498(49)	426(48)	9(33)	-11(36)	37(37)
C18	467(63)	512(59)	481(70)	-30(47)	-107(52)	90(49)
C19	450(64)	1012(91)	666(82)	-18(60)	-29(59)	68(68)
C20	636(70)	732(75)	400(64)	-65(57)	20(56)	186(55)
C21	429(58)	623(66)	442(64)	-110(49)	26(50)	42(52)
C22	593(76)	1137(101)	687(87)	-100(66)	131(66)	25(74)
N6	339(44)	617(52)	511(55)	10(36)	34(39)	44(42)
W1	727(49)	766(52)	1207(67)	-157(44)	-256(47)	561(52)

$U_{i,j}$ values have been multiplied by 10^4

The form of the displacement factor is:

$$\exp -2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}k\ell b^*c^*)$$

Table S3. Complete Distances and Angles for
Bis(3,5-dimethylpyrazolium)(5,5'-dimethyl-2,2'-dipyridyl) Platinum(II).

		Distance(Å)			Distance(Å)
Pt	-N1	2.018(7)	C16	-C17	1.517(15)
Pt	-N2	2.000(7)	C16	-N4	1.326(12)
Pt	-N3	1.975(7)	C17	-H17A	0.951
Pt	-N5	1.990(7)	C17	-H17B	0.946
N1	-C1	1.327(12)	C17	-H17C	0.950
N1	-C6	1.376(11)	N5	-C18	1.338(12)
C1	-C2	1.389(14)	N5	-N6	1.386(10)
C1	-H1	0.946	C18	-C19	1.489(14)
C2	-C3	1.381(14)	C18	-C20	1.383(14)
C2	-H2	0.951	C19	-H19A	0.938
C3	-C4	1.501(15)	C19	-H19B	0.956
C3	-C5	1.388(14)	C19	-H19C	0.951
C4	-H4A	0.955	C20	-C21	1.404(14)
C4	-H4B	0.956	C20	-H20	0.947
C4	-H4C	0.939	C21	-C22	1.486(15)
C5	-C6	1.371(13)	C21	-N6	1.342(12)
C5	-H5	0.945	C22	-H22A	0.947
C6	-C7	1.471(12)	C22	-H22B	0.940
C7	-C8	1.379(13)	C22	-H22C	0.962
C7	-N2	1.363(11)	O	-C23	1.367
C8	-C9	1.391(14)	O	-C26	1.386
C8	-H8	0.947	C23	-C24	1.345
C9	-C10	1.512(15)	C23	-H23A	0.950
C9	-C11	1.384(14)	C23	-H23B	0.950
C10	-H10A	0.954	C24	-C25	1.381
C10	-H10B	0.945	C24	-H24A	0.950
C10	-H10C	0.951	C24	-H24B	0.950
C11	-C12	1.412(14)	C25	-C26	1.298
C11	-H11	0.950	C25	-H25A	0.950
C12	-N2	1.341(12)	C25	-H25B	0.950
C12	-H12	0.952	C26	-H26A	0.950
N3	-C13	1.337(11)	C26	-H26B	0.950
N3	-N4	1.379(10)			
C13	-C14	1.485(13)			
C13	-C15	1.384(13)			
C14	-H14A	0.959			
C14	-H14B	0.942			
C14	-H14C	0.951			
C15	-C16	1.383(14)			
C15	-H15	0.958			

Table S3 (.Cont.)

Angle(°)		Angle(°)	
H19B -C19 -H19A	110.0	H26B -C26 -H26A	109.5
H19C -C19 -H19A	110.4		
H19C -C19 -H19B	108.9		
C21 -C20 -C18	106.5(9)		
H20 -C20 -C18	126.4		
H20 -C20 -C21	127.1		
C22 -C21 -C20	129.7(9)		
N6 -C21 -C20	108.9(8)		
N6 -C21 -C22	121.4(9)		
H22A -C22 -C21	109.6		
H22B -C22 -C21	110.0		
H22C -C22 -C21	108.7		
H22B -C22 -H22A	110.6		
H22C -C22 -H22A	108.7		
H22C -C22 -H22B	109.3		
C21 -N6 -N5	106.8(7)		
C26 -O -C23	107.7		
C24 -C23 -O	106.8		
H23A -C23 -O	110.1		
H23B -C23 -O	110.1		
H23A -C23 -C24	110.1		
H23B -C23 -C24	110.1		
H23B -C23 -H23A	109.5		
C25 -C24 -C23	108.2		
H24A -C24 -C23	109.8		
H24B -C24 -C23	109.8		
H24A -C24 -C25	109.8		
H24B -C24 -C25	109.8		
H24B -C24 -H24A	109.5		
C26 -C25 -C24	109.0		
H25A -C25 -C24	109.6		
H25B -C25 -C24	109.6		
H25A -C25 -C26	109.6		
H25B -C25 -C26	109.6		
H25B -C25 -H25A	109.5		
C25 -C26 -O	108.0		
H26A -C26 -O	109.8		
H26B -C26 -O	109.8		
H26A -C26 -C25	109.8		
H26B -C26 -C25	109.8		

Table S3 (Cont.)

Angle(°)				Angle(°)			
N1	-Pt	-N2	80.4(3)	H10B	-C10	-H10A	109.6
N1	-Pt	-N3	94.8(3)	H10C	-C10	-H10A	109.0
N1	-Pt	-N4	84.4(2)	H10C	-C10	-H10B	109.8
N2	-Pt	-N3	175.2(3)	C12	-C11	-C9	118.8(9)
N2	-Pt	-N4	153.3(2)	H11	-C11	-C9	120.2
N3	-Pt	-N4	23.9(2)	H11	-C11	-C12	121.1
C6	-N1	-C1	118.2(7)	N2	-C12	-C11	122.2(8)
C2	-C1	-N1	122.8(9)	H12	-C12	-C11	118.7
H1	-C1	-N1	118.4	H12	-C12	-N2	119.1
H1	-C1	-C2	118.8	C12	-N2	-C7	117.9(7)
C3	-C2	-C1	119.6(9)	N4	-N3	-C13	109.7(7)
H2	-C2	-C1	120.1	C14	-C13	-N3	123.2(8)
H2	-C2	-C3	120.3	C15	-C13	-N3	108.2(8)
C4	-C3	-C2	121.7(9)	C15	-C13	-C14	128.6(9)
C5	-C3	-C2	117.7(9)	H14A	-C14	-C13	109.0
C5	-C3	-C4	120.7(9)	H14B	-C14	-C13	110.0
H4A	-C4	-C3	109.1	H14C	-C14	-C13	109.8
H4B	-C4	-C3	109.1	H14B	-C14	-H14A	109.4
H4C	-C4	-C3	110.3	H14C	-C14	-H14A	108.6
H4B	-C4	-H4A	108.5	H14C	-C14	-H14B	110.1
H4C	-C4	-H4A	109.9	C16	-C15	-C13	105.0(9)
H4C	-C4	-H4B	109.8	H15	-C15	-C13	127.0
C6	-C5	-C3	120.7(9)	H15	-C15	-C16	128.0
H5	-C5	-C3	119.5	C17	-C16	-C15	129.2(9)
H5	-C5	-C6	119.8	N4	-C16	-C15	111.2(8)
C5	-C6	-N1	121.1(8)	N4	-C16	-C17	119.6(8)
C7	-C6	-N1	113.8(7)	H17A	-C17	-C16	108.7
C7	-C6	-C5	125.2(8)	H17B	-C17	-C16	109.8
C8	-C7	-C6	122.3(8)	H17C	-C17	-C16	109.4
N2	-C7	-C6	114.6(7)	H17B	-C17	-H17A	109.7
N2	-C7	-C8	123.2(8)	H17C	-C17	-H17A	109.4
C9	-C8	-C7	118.7(9)	H17C	-C17	-H17B	109.8
H8	-C8	-C7	121.8	C16	-N4	-N3	105.9(7)
H8	-C8	-C9	119.5	N6	-N5	-C18	110.0(7)
C10	-C9	-C8	120.1(9)	C19	-C18	-N5	123.2(8)
C11	-C9	-C8	119.3(9)	C20	-C18	-N5	107.7(8)
C11	-C9	-C10	120.7(9)	C20	-C18	-C19	128.9(9)
H10A	-C10	-C9	109.1	H19A	-C19	-C18	109.7
H10B	-C10	-C9	109.9	H19B	-C19	-C18	108.7
H10C	-C10	-C9	109.5	H19C	-C19	-C18	109.1

Table S4. Observed and Calculated Structure Factors for
 Bis(3,5-dimethylpyrazolium)(5,5'-dimethyl-2,2'-dipyridyl) Platinum(II)

The columns contain, in order, k , $10F_{obs}$, $10F_{calc}$ and $10\left(\frac{F_{obs}^2 - F_{calc}^2}{\sigma F_{obs}^2}\right)$. A minus sign preceding F_{obs} indicates that F_{obs}^2 is negative.

Bis(pyrazolium)dipyridyl Platinum Complex.

Page 1

-10 k 1	-9 k 5	-8 k 3	10 278 137 23
1 530 449 25	0 426 492 -15	1 495 548 -21	11 615 599 5
2 403 397 1	1 379 392 -3	2 739 733 2	-8 k 8
3 639 597 15	2 -71 84 -5	3 713 714 0	0 837 857 -5
4 177 88 10	3 289 306 -3	4 89 143 -6	1 237 246 -1
5 169 210 -6	4 526 504 7	5 246 178 14	2 66 164 -10
-10 k 2	5 227 261 -7	6 625 605 8	3 162 160 0
0 158 32 8	6 257 278 -4	7 635 609 10	4 664 663 0
1 578 566 4	7 -81 16 -3	8 362 332 9	5 296 287 2
2 193 11 15	8 514 483 10	9 187 175 2	6 315 322 -1
3 367 404 -10	9 389 424 -10	10 427 422 1	7 208 163 7
4 222 154 10	-9 k 6	11 596 592 1	8 468 479 -3
-10 k 3	1 456 432 7	12 391 385 1	9 294 282 2
1 325 327 0	2 106 170 -7	13 -49 107 -6	10 367 408 -5
2 521 526 -1	3 636 613 8	-8 k 4	-8 k 9
3 328 319 2	4 99 107 0	0 1079 1100 -7	1 219 146 10
-9 k 1	5 75 175 -10	1 -111 16 -6	2 770 718 19
0 472 428 10	6 255 232 4	2 202 137 11	3 33 99 -3
1 517 577 -23	7 691 629 22	3 158 23 12	4 258 278 -4
2 54 73 -1	8 -165 36 -12	4 839 852 -5	5 -97 116 -10
3 393 433 -13	-9 k 7	5 35 113 -6	6 591 564 9
4 494 480 5	0 317 332 -2	6 362 347 4	7 218 239 -3
5 593 614 -8	1 527 501 8	7 139 44 8	8 290 337 -11
6 284 218 14	2 146 65 7	8 741 748 -2	-8 k 10
7 164 183 -3	3 284 339 -12	9 -33 51 -1	0 498 386 22
8 379 378 0	4 227 259 -5	10 553 526 10	1 412 440 -8
9 623 598 9	5 523 547 -7	11 129 17 7	2 -54 98 -5
10 330 291 9	6 204 157 6	12 546 518 9	3 196 239 -7
11 193 6 16	-9 k 8	13 32 38 0	4 345 333 2
-9 k 2	1 197 146 6	14 550 541 3	5 381 437 -15
1 590 561 3	2 609 618 -3	-8 k 5	-7 k 1
2 154 119 4	3 247 211 6	1 460 455 1	0 841 910 -25
3 793 777 6	-8 k 1	2 637 655 -7	1 815 804 5
4 141 11 9	1 562 544 7	3 282 283 0	2 268 176 24
5 296 291 1	2 761 774 -6	4 273 308 -9	3 562 560 1
6 75 42 1	3 744 747 -1	5 229 212 3	4 725 649 36
7 787 750 15	4 257 248 2	6 546 588 -16	5 959 985 -13
8 -84 16 -3	5 398 394 1	7 452 510 -21	6 276 275 0
9 103 124 -2	6 587 540 19	8 320 258 15	7 329 275 17
10 180 114 8	7 721 724 -1	9 129 47 6	8 663 683 -9
11 661 672 -4	8 234 246 -2	10 499 509 -3	9 800 810 -4
-9 k 3	9 235 107 21	11 465 460 1	10 231 196 8
0 694 652 11	10 372 394 -7	12 417 443 -8	11 150 34 12
1 461 421 12	11 766 743 10	13 -111 43 -6	12 348 229 32
2 277 105 27	12 491 459 11	-8 k 6	13 683 674 4
3 340 327 3	13 83 93 0	0 193 42 11	14 481 459 7
4 624 608 6	14 159 128 3	1 -609 626 -6	15 294 244 11
5 398 434 -11	15 457 455 0	2 -216 97 -30	16 206 154 8
6 260 220 8	-8 k 2	3 261 295 -8	17 385 431 -14
7 -149 96 -15	0 97 133 -3	4 212 246 -7	-7 k 2
8 474 485 -3	1 885 912 -12	5 658 697 -16	1 720 732 -5
9 474 436 12	2 -118 19 -8	6 -139 39 -10	2 113 52 6
10 348 323 6	3 522 548 -10	7 109 212 -15	3 970 997 -14
-9 k 4	4 110 18 6	8 219 220 0	4 -20 91 -5
1 -41 36 -1	5 882 905 -11	9 673 677 -1	5 719 706 6
2 789 822 -13	6 129 12 9	10 221 83 18	6 332 226 31
3 -73 5 -2	7 284 319 -10	11 -152 23 -11	7 1179 1170 4
4 137 105 3	8 192 31 18	12 261 115 22	8 174 97 12
5 -138 40 -10	9 829 846 -7	-8 k 7	9 232 207 5
6 519 518 0	10 124 15 7	1 442 467 -8	10 88 129 -5
7 -72 25 -2	11 -66 37 -2	2 245 278 -7	11 944 921 10
8 407 401 1	12 161 70 9	3 676 684 -3	12 163 61 12
9 -107 3 -5	13 762 746 6	4 52 92 -2	13 263 252 2
10 544 537 2	14 139 22 8	5 223 280 -12	14 -04 86 -8
	15 168 221 -9	6 306 304 0	15 701 651 20
		7 565 564 7	16 -129 55 -9
		8 224 276 -11	17 252 268 -3
		9 67 148 -7	

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-7 k 3	-7 k 7	2 330 375 -11	4 1528 1539 -5
0 1066 1061 1	0 467 508 -11	3 365 339 6	5 347 347 0
1 827 830 -1	1 580 532 21	4 -254 49 -30	6 745 769 -12
2 259 236 6	2 -129 29 -9	5 195 182 1	7 128 5 10
3 322 363 -14	3 212 213 0	-6 k 1	8 972 965 3
4 856 835 10	4 244 334 -25	1 483 508 -12	9 280 299 -6
5 904 877 13	5 811 812 0	2 840 859 -11	10 748 749 0
6 474 467 2	6 293 318 -7	3 1045 991 29	11 -109 21 -7
7 156 190 -6	7 359 386 -8	4 212 177 9	12 422 440 -6
8 445 449 -1	8 62 184 -15	5 522 498 12	13 -109 35 -7
9 796 801 -2	9 586 593 -2	6 793 794 0	14 687 679 3
10 267 305 -11	10 183 184 0	7 1244 1259 -7	15 -160 77 -17
11 138 63 8	11 -202 37 -22	8 358 345 5	16 223 275 -12
12 389 392 -1	12 -48 141 -10	9 147 87 9	17 -102 70 -7
13 558 574 -6	13 648 618 11	10 836 850 -7	18 583 590 -2
14 299 359 -17	14 176 190 -2	11 674 639 16	19 -88 30 -4
15 205 223 -3	-7 k 8	12 255 254 0	-6 k 5
16 280 234 9	1 212 254 -9	13 98 136 -5	1 368 402 -13
17 334 309 6	2 695 700 -1	14 401 363 13	2 1251 1261 -4
-7 k 4	3 365 349 4	15 731 731 0	3 459 478 -8
1 176 204 -5	4 319 331 -3	16 617 565 20	4 430 474 -19
2 1167 1173 -3	5 178 207 -5	17 338 383 -14	5 366 370 -1
3 320 344 -8	6 838 830 3	18 184 204 -3	6 1014 1048 -17
4 361 384 -8	7 244 217 5	19 464 495 -10	7 612 630 -8
5 146 159 -2	8 442 451 -3	-6 k 2	8 628 632 -2
6 1086 1127 -20	9 -130 177 -24	0 220 268 -15	9 -177 68 -24
7 -107 22 -7	10 348 359 -3	1 1054 1051 1	10 668 622 20
8 618 600 8	11 370 385 -4	2 -124 106 -20	11 422 398 8
9 -144 30 -13	12 399 398 0	3 974 969 2	12 522 539 -7
10 660 643 7	13 152 26 9	4 239 111 29	13 -30 26 0
11 212 118 15	-7 k 9	5 1475 1464 5	14 441 397 14
12 601 604 0	0 1004 976 8	6 173 133 8	15 458 444 4
13 199 153 7	1 230 129 16	7 361 393 -13	16 627 613 5
14 397 378 5	2 201 209 -1	8 164 28 17	17 246 204 8
15 148 36 9	3 44 124 -6	9 1351 1330 10	18 77 130 -5
16 609 578 11	4 885 855 12	10 -67 134 -15	-6 k 6
-7 k 5	5 295 274 5	11 -84 48 -6	0 294 370 -19
0 1021 1088 -23	6 347 360 -3	12 126 96 4	1 690 684 3
1 452 406 16	7 112 14 5	13 928 901 12	2 149 172 -4
2 152 191 -7	8 566 528 13	14 177 15 17	3 712 739 -13
3 416 448 -12	9 143 197 -8	15 272 248 6	4 416 429 -5
4 802 812 -4	10 472 444 8	16 155 131 3	5 1032 1056 -12
5 517 522 -2	11 -196 43 -19	17 757 716 17	6 231 258 -7
6 361 349 3	12 316 342 -6	18 75 47 1	7 344 394 -18
7 330 234 25	-7 k 10	19 239 269 -11	8 218 241 -5
8 578 590 -5	1 377 425 -14	-6 k 3	9 987 1024 -18
9 503 525 -8	2 460 435 8	1 823 827 -2	10 201 198 0
10 464 468 -1	3 488 497 -2	2 1070 1082 -6	11 -154 24 -14
11 -141 89 -15	4 107 160 -6	3 906 940 -18	12 159 98 6
12 418 410 2	5 293 327 -8	4 342 332 3	13 834 808 11
13 431 465 -12	6 353 379 -7	5 557 605 -24	14 193 190 0
14 502 505 -1	7 595 645 -18	6 975 986 -5	15 223 198 4
15 -146 119 -17	8 129 163 -4	7 1080 1057 11	16 137 136 0
16 228 207 3	9 56 10 1	8 690 669 10	17 655 626 10
-7 k 6	10 269 261 1	9 108 118 -1	-6 k 7
1 565 589 -10	-7 k 11	10 345 319 9	1 332 366 -11
2 203 70 18	0 -185 21 -11	11 784 814 -14	2 403 401 0
3 548 501 18	1 577 534 14	12 470 456 5	3 813 860 -22
4 192 220 -6	2 -118 34 -6	13 208 178 6	4 -106 115 -15
5 526 567 -17	3 280 328 -11	14 342 336 1	5 510 525 -6
6 236 218 4	4 89 68 1	15 672 631 17	6 450 456 -2
7 875 871 1	5 568 615 -17	16 434 444 -3	7 886 896 -4
8 -128 71 -12	6 -83 43 -3	17 251 253 0	8 283 294 -3
9 132 135 0	7 185 160 3	18 122 139 -2	9 149 173 -4
10 288 203 19	8 -171 44 -13	19 309 296 3	10 33 201 -21
11 770 796 -12	-7 k 12	-6 k 4	11 713 714 0
12 201 220 -3	1 260 273 -2	0 1546 1547 0	12 117 178 -9
13 162 76 9		1 279 274 1	13 146 91 6
14 230 58 21		2 131 195 -13	14 147 151 0
15 631 611 7		3 229 145 19	15 776 723 20
			16 244 282 -8
			17 222 266 -13

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-6 k	8	5 536 508 9	10 349 391 -17	18 -141 4 -9
0 560 538 6	6 273 247 5	11 -112 20 -9	19 394 439 -13	
1 152 249 -21	7 176 145 4	12 223 244 -5		
2 236 211 5	8 330 354 -6	13 639 602 16	-5 k	7
3 328 345 -5	9 424 382 11	14 652 638 6	0 836 813 8	
4 903 929 -12	10 274 285 -2	15 -158 107 -22	1 907 891 8	
5 329 364 -11	-6 k 13	16 253 172 17	2 228 182 11	
6 343 367 -8	1 45 74 -1	17 670 667 1	3 828 796 16	
7 -177 193 -40	2 619 605 4	18 501 496 1	4 408 400 3	
8 648 647 0	3 -248 79 -32	19 217 229 -2	5 1129 1141 -6	
9 343 368 -8	4 21 179 -13	20 -65 148 -12	6 -100 108 -14	
10 482 468 4	5 -40 0 0	-5 k 4	7 209 221 -3	
11 95 17 4	6 632 564 22	1 316 257 21	8 239 322 -26	
12 333 306 7	7 151 49 8	2 1714 1699 7	9 1023 1026 -1	
13 367 364 1	-5 k 1	3 244 244 0	10 182 140 7	
14 531 538 -2	0 513 512 0	4 505 504 0	11 -8 112 -7	
15 103 35 4	1 753 783 -18	5 113 127 -2	12 242 307 -18	
16 157 208 -7	2 402 376 13	6 1396 1393 1	13 766 736 13	
-6 k 9	3 526 531 -2	7 241 112 29	14 294 313 -5	
1 -122 40 -9	4 973 994 -13	8 800 801 0	15 -15 159 -13	
2 907 920 -8	5 1079 1081 -1	9 136 63 9	16 -93 100 -9	
3 120 226 -19	6 563 510 28	10 853 849 2	17 628 596 12	
4 246 225 4	7 327 326 0	11 288 283 1	18 186 235 -9	
5 -130 50 -10	8 1011 973 21	12 710 696 6	-5 k 8	
6 778 804 -11	9 1128 1150 -12	13 144 169 -4	1 79 167 -13	
7 175 209 -6	10 587 631 -23	14 506 468 15	2 955 929 12	
8 426 418 2	11 -47 5 -1	15 252 178 16	3 616 574 18	
9 128 138 -1	12 336 394 -23	16 737 729 3	4 375 369 2	
10 485 492 -2	13 950 935 7	17 128 133 0	5 -91 79 -9	
11 -159 58 -14	14 543 496 20	18 137 173 -5	6 936 969 -16	
12 459 487 -9	15 197 264 -17	19 43 18 0	7 466 437 11	
13 -163 105 -18	16 240 225 3	20 482 504 -7	8 405 427 -8	
14 516 436 25	17 660 662 0	-5 k 5	9 -141 88 -17	
15 -34 88 -3	18 603 617 -5	0 1222 1217 1	10 497 510 -5	
-6 k 10	19 368 366 0	1 631 588 22	11 281 305 -6	
0 408 456 -12	20 197 53 16	2 -90 12 -6	12 535 544 -3	
1 525 502 8	21 309 320 -2	3 264 291 -9	13 -113 12 -7	
2 -139 57 -12	-5 k 2	4 1408 1407 0	14 334 394 -18	
3 408 412 -1	1 1173 1228 -31	5 601 595 3	15 395 371 7	
4 601 594 2	2 166 127 9	6 768 766 0	16 522 523 0	
5 686 707 -6	3 1253 1235 10	7 358 334 9	17 -117 136 -15	
6 164 205 -7	4 287 262 9	8 974 1000 -13	18 184 143 5	
7 130 155 -3	5 511 497 7	9 618 632 -7	-5 k 9	
8 449 452 -1	6 76 27 4	10 847 826 10	0 609 608 0	
9 593 592 0	7 1665 1677 -6	11 130 103 3	1 -149 75 -17	
10 230 264 -7	8 399 365 15	12 469 425 17	2 226 216 2	
11 -111 96 -10	9 332 368 -15	13 519 518 0	3 -102 140 -18	
12 216 267 -10	10 -44 102 -9	14 565 584 0	4 1008 993 6	
13 433 458 -7	11 1086 1039 24	15 154 142 1	5 151 203 -10	
-6 k 11	12 162 141 4	16 249 257 -1	6 354 349 1	
1 414 495 -28	13 151 205 -12	17 155 253 -19	7 231 262 -7	
2 -59 63 -3	14 151 126 4	18 630 579 19	8 753 767 -6	
3 773 747 10	15 1001 1006 -2	19 225 173 8	9 -27 122 -8	
4 -70 60 -4	16 216 130 16	20 -97 13 -4	10 410 479 -26	
5 309 317 -2	17 521 509 4	-5 k 6	11 134 13 9	
6 102 79 1	18 181 18 16	1 890 891 0	12 449 441 2	
7 779 766 5	19 633 657 -9	2 542 567 -12	13 143 240 -17	
8 97 128 -3	20 23 41 0	3 1207 1223 -7	14 573 531 15	
9 -212 37 -22	21 282 339 -14	4 -25 53 -2	15 -106 167 -18	
10 -68 16 -2	-5 k 3	5 566 634 -35	16 315 296 4	
11 567 543 14	0 1435 1402 13	6 364 349 13	17 85 52 1	
12 -81 36 -3	1 689 719 -17	7 1286 1300 -7	-5 k 10	
-6 k 12	2 392 431 -19	8 273 288 -4	1 272 319 -14	
0 427 453 -5	3 952 956 -2	9 -123 138 -23	2 609 641 -14	
1 350 357 -2	4 1104 1107 -1	10 262 282 -6	3 629 615 5	
2 67 77 0	5 1233 1219 7	11 959 957 0	4 -175 78 -21	
3 314 328 -3	6 652 618 18	12 306 327 -6	5 340 378 -12	
4 432 485 -17	7 420 393 12	13 188 200 -2	6 485 473 4	
	8 828 838 -5	14 155 164 -1	7 650 707 -25	
	9 968 982 2	15 771 741 13	8 244 247 0	
		16 356 350 1	9 -100 60 -7	
		17 325 327 0		

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10	478	479	0	8	549	555	-3	9	263	293	-11	15	760	747	5
11	570	556	5	9	169	148	5	10	886	904	-10	16	167	214	-9
12	362	321	11	10	806	801	2	11	113	70	5	17	292	305	-3
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6	201	257	-13	2	515	534	-6	9	931	931	0	9	903	896	3
7	-152	35	-14	3	75	219	-17	10	297	271	7	10	127	40	7
8	486	517	-12	4	90	213	-15	11	182	96	12	11	-225	25	-27
9	532	559	-10	5	295	259	7	12	194	135	10	12	-127	9	-7
10	362	327	10	6	591	591	0	13	844	839	2	13	647	590	20
11	-180	55	-19					14	318	331	-3	14	-137	8	-8
12	360	371	-3	7	k	0		15	263	228	7				
13	528	552	-8					16	61	8	1	7	k	8	
14	442	429	4	1	201	50	34	17	536	532	1				
15	-61	66	-3	2	1227	1221	3					1	501	499	0
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	6	k	9	4	499	484	9					3	441	468	-9
				5	381	357	13	1	290	306	-4	4	148	203	-9
1	-66	64	-4	6	1013	1018	-3	2	1034	1061	-13	5	240	272	-7
2	789	788	0	7	405	412	-3	3	232	136	19	6	393	371	6
3	-245	40	-37	8	557	580	-15	4	398	414	-6	7	656	689	-13
4	-67	75	-5	9	271	265	2	5	481	490	-3	8	91	179	-11
5	-62	142	-12	10	686	699	-8	6	707	696	5	9	99	12	4
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7	165	210	-8	12	658	644	8	8	497	462	13	11	563	544	6
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9	-96	26	-5	14	382	358	10	10	631	612	7	13	122	135	-1
10	582	583	0	15	131	183	-11	11	502	463	14				
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12	557	539	6	17	72	78	0	13	-91	27	-4				
13	113	132	-2					14	252	234	4	0	822	826	-1
14	348	363	-4	7	k	1		15	407	409	0	1	218	141	12
15	77	126	-4					16	539	515	8	2	64	126	-5
	6	k	10	0	1243	1256	-4					3	-177	67	-18
				1	365	340	8	7	k	5		4	631	620	4
0	628	664	-10	2	441	469	-12					5	113	153	-2
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2	-92	62	-6	4	1101	1102	0	1	174	192	-3	7	-148	40	-11
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4	758	701	23	6	584	570	6	3	93	16	4	9	239	127	17
5	506	464	14	7	152	204	-11	4	977	1021	-21	10	486	421	19
6	270	286	-4	8	553	515	16	5	249	190	13	11	78	26	2
				9	567	524	18	6	499	498	0	12	270	368	-24
				10	615	623	-3	7	170	43	14				

7	k	10		7	335	302	9					1	474	441	10
				8	172	131	6					2	342	374	-9
1	182	217	-6	9	666	662	1	1	647	610	13	3	700	718	-7
2	576	570	2	10	367	391	-7	2	145	18	9	4	13	94	-4
3	303	335	-8	11	140	85	6	3	779	798	-7	5	248	287	-9
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6	513	490	7	14	298	220	16	6	141	35	8	8	59	204	-18
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8	354	321	8					8	-35	48	-1	10	332	256	17
9	-223	66	-25	8	k	s		9	235	216	3	11	617	607	3
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7	k	11		2	288	252	9	8	k	8		9	k	3	
				3	824	813	5					0	235	65	5
0	250	278	-4	4	-38	54	-2	0	467	477	-2	1	626	584	5
1	427	434	-1	5	389	353	11	1	554	563	-3	2	89	87	0
2	-160	15	-11	6	298	217	19	2	157	88	7	3	426	43	-1
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3	385	417	-8	0	833	813	6	2	752	773	-8	2	595	614	-7
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7	150	96	10	11	-127	90	-12	1	187	229	-6	0	764	768	0
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9	283	224	20	13	482	375	32	3	79	215	-16	2	82	35	2
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14	317	292	6	2	-139	66	-12	4	759	756	1	3	345	366	-5
15	157	217	-9	3	362	381	-5	5	352	365	-3	4	53	58	0
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8	k	2		5	525	554	-10	7	239	152	15				
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2	165	51	13	8	439	479	-13	10	511	474	12	2	505	379	24
3	434	420	5	9	545	489	19	11	236	18	23				
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5	868	817	23	11	136	51	7	9	k	2					
6	178	190	-2	12	314	290	5								
								8	k	7					

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0	691	697	- 2	10	k	1						4	314	255	13
1	203	142	13					10	k	2					
2	131	81	6	1	288	195	17					10	k	3	
3	215	140	16	2	645	651	- 2	0	205	243	- 4				
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