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卟咯锰(III)与锰(V)-氧配合物与含氮配体的轴向配位性质

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摘要: 采用密度泛函理论(DFT)的BP86方法对含氮配体咪唑、甲基咪唑、异丙基咪唑和吡啶与5,10,15-三(五氟苯基)卟咯锰[(TPFC)Mn^{III}]和5,10,15-三(五氟苯基)卟咯锰氧[(TPFC)Mn^VO]的轴向配位性质进行理论研究. 计算结果表明配体能与五重态下的(TPFC)Mn^{III}形成有效的轴向配位作用, 结合能绝对值次序为: 咪唑>4-甲基咪唑>吡啶, 与实验结果一致. 另外, 结合能和轴向配位键长数据显示, 这些配体不能与基态(单重态)或三重态(TPFC)Mn^VO中的Mn^V原子形成有效的轴向配位作用, 自然键轨道(NBO)分析表明其Mn^V没有空的3d轨道来接受配体的孤对电子, 但配体可与三重态下的(TPFC)Mn^VO形成弱的配位作用.

关键词: 卟咯; 锰; 锰-氧配合物; 密度泛函理论; 轴向配位

中图分类号: O641

Axial Coordination Behavior of Corrole Mn^{III} and Mn^VO Complexes with N-Based Ligands

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Abstract: The axial coordination behavior of the 5,10,15-tris(pentafluorophenyl)corrole manganese [(TPFC)Mn^{III}] and 5,10,15-tris(pentafluorophenyl)corrole manganese(V)-oxo [(TPFC)Mn^VO] complexes with N-based ligands, such as imidazole, methylimidazole, isopropylimidazole, and pyridine, were investigated using density functional theory (DFT) at BP86 level. The results show these N-based ligands can form a stable axial coordination complex with (TPFC)Mn^{III} in its quintet state. The coordination binding strength followed the order imidazole>4-methylimidazole>pyridine, which is in agreement with experimental results. The binding energy and the large distance between the Mn and N atom of the ligands indicates that (TPFC)Mn^VO cannot form an effective coordination bond in its singlet or triple state. Natural bond orbital (NBO) analysis indicates that the 3d orbitals of the Mn atom in (TPFC)Mn^VO are fully occupied, and there are no empty 3d orbitals to accept lone pair electrons from the ligands. However, there is a weak coordination interaction between the ligands and (TPFC)Mn^VO in its triplet state.

Key Words: Corrole; Manganese; Manganese-oxo complex; Density functional theory; Axial coordination

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1 引言

卟咯(corrole)是一种四吡咯大环化合物. 与卟啉相比, 卟咯中的两个吡咯环直接相连, 导致对称性降低, 环内空腔更小, 能与高价金属形成稳定的配合物.^{1,2} 近年来, 由于合成方法的突破,^{3,4} corrole大环化合物各方面的研究有了很快的发展,^{5,6} 已经成为当今卟啉化学的热门课题. 卟咯锰配合物在催化氧化方面存在着广泛的应用,^{5,7} 可以催化烯烃的环氧化、^{8,9} 烷烃的羟基化¹⁰和硫醚的氧化¹¹等反应. 2000年, Gross等⁹报道在亚碘酰苯作为氧化剂条件下, 卟咯锰配合物可以催化苯乙烯的环氧化反应, 并发现反应历程中有卟咯 Mn^{VO} 中间体生成. 卟咯 Mn^{VO} 虽然较稳定, 但也会逐渐衰变为卟咯 Mn^{III} .^{9,12} Collman等¹³认为卟咯 Mn^{VO} 是催化氧化活性中间体之一, 而Gross等¹¹则认为卟咯 Mn^{VO} 通过歧化反应生成更高价态的卟咯 Mn^{VO} 也是催化氧化活性中间体. 我们最近的研究工作¹⁴发现5,10,15-三(2,4,6-三苯基苯基)卟咯锰氧配合物[(TPPFC) Mn^{VO}]在苯乙烯过量的情况下, 其衰变速率加快, 表明(TPPFC) Mn^{VO} 能与苯乙烯直接反应, 卟咯 Mn^{VO} 的确是催化氧化活性中间体. 卟咯 Mn^{VO} 有一定的稳定性, 甚至可以分离纯化, 并通过系列光谱进行了表征.^{9,15} 拉曼光谱实验和理论计算研究发现卟咯 Mn^{VO} 的锰与氧之间形成的是由1个 σ 键和2个 π 键组成的三键结构.^{14,16} 目前, 围绕着如何提高催化氧

化能力的研究集中在卟咯 Mn^{VO} 及其卟咯 Mn^{III} 配合物物种的结构与性质上.

配体与锰卟啉轴向配位对其催化性能有重要的调节作用,^{12,17} 但有关配体与锰卟咯的轴向作用的研究较少. 对咪唑、4-甲基咪唑和吡啶与(TPFC) Mn^{III} 配位常数的研究中发现轴向配位常数大小次序为: 咪唑>4-甲基咪唑>吡啶,¹⁸ 理论上带供电子甲基的4-甲基咪唑配位能力应大于咪唑, 对此实验现象仍需进一步给出合理的解释. 另一方面在配体存在下, (TPFC) Mn^{VO} 的催化氧化¹²和降解¹⁸的速率明显加快, 但其机理成因目前尚未清楚, 相关配体与(TPFC) Mn^{VO} 的轴向配位性质尚待深入的研究. 为了研究配体与卟咯锰配合物的轴向配位作用及不同配体对其的影响以及卟咯 Mn^{VO} 与配体作用的情况, 本文采用DFT方法对咪唑、甲基咪唑、异丙基咪唑和吡啶分别与(TPFC) Mn^{VO} 和(TPFC) Mn^{III} 的轴向作用进行量子化学计算, 从电子效应和空间效应两方面合理解释轴向配位常数的次序, 同时对配体与不同多重度下卟咯 Mn^{VO} 间的作用机理进行理论分析.

2 计算方法

为了选择最优的计算方法, 以卟咯锰配合物[(OEC) Mn^{III} (Py)] (OEC: 八乙基卟咯; Py: 吡啶)的单晶结构¹⁹为对象(结构如图1所示), 分别采用DFT的

图1 (OEC) Mn^{III} (Py)、(TPFC) Mn^{III} (L)和(TPFC) Mn^{VO} (L)的分子结构

Fig.1 Molecular structures of (OEC) Mn^{III} (Py), (TPFC) Mn^{III} (L), and (TPFC) Mn^{VO} (L)

Im: imidazole; 4-MI: 4-methyl imidazole; Py: pyridine; 2-MI: 2-methyl imidazole; 5-MI: 5-methyl imidazole;

4-IPI: 4-isopropyl imidazole; 2-IPI: 2-isopropyl imidazole; 5-IPI: 5-isopropyl imidazole

表1 五重态下(OEC)Mn^{III}(Py)在DFT方法下优化的几何参数和实验值

Table 1 DFT optimized and experimental parameters of (OEC)Mn ^{III} (Py) in the quintet state				
Parameter	B3LYP	BP86	PBE0	Expt. ¹⁹
$d_{\text{Mn-N1}}/\text{nm}$	0.1915	0.1916	0.1915	
$d_{\text{Mn-N2}}/\text{nm}$	0.1915	0.1916	0.1914	
$d_{\text{Mn-N3}}/\text{nm}$	0.1934	0.1932	0.1931	
$d_{\text{Mn-N4}}/\text{nm}$	0.1935	0.1932	0.1931	
$d_{\text{Mn-N}}^{\text{a}}/\text{nm}$	0.1925	0.1924	0.1923	0.1917
$d_{\text{Mn-L}}^{\text{b}}/\text{nm}$	0.2349	0.2316	0.2319	0.2277
$\Delta d(\text{N4})/\text{nm}$	0.0223	0.0213	0.0202	0.0256

^aaverage bonding lengths of four Mn—N bonds; ^bdistances of coordination bond; ^cdistances between Mn atom and the mean plane of the four nitrogen atoms in pyrroles

B3LYP、BP86、PBE0方法, Mn原子采用LanL2DZ基组, 非金属原子采用6-31G(*d,p*)基组, 多重度为五, 进行几何优化计算. 优化的主要几何结构数据见表1, 结果显示三种方法中BP86方法计算的配位键的键长 $d_{\text{Mn-L}}$ (0.2316 nm)与实验值(0.2277 nm)¹⁹最接近, 说明该方法较准确. 故本文采用BP86方法, Mn原子采用LanL2DZ基组, 非金属原子采用6-31G(*d,p*)基组对所有的分子几何结构优化计算, 并设计了8个轴向作用的配体, 包括咪唑、吡啶、3个单甲基取代咪唑和3个单异丙基取代咪唑(见图1). 配体与(TPFC)Mn^{III}或(TPFC)Mn^VO形成轴向配位(见图1).

卟咯Mn^VO单重态下最为稳定,¹⁶ 而卟咯Mn^{III}以五重态为最稳定.²⁰ 在配体存在下, 上述体系的最稳定组态是否改变? 由于研究的配体较多, 为节省计算量, 计算时选取已被较广泛研究的配体吡啶为代表, 计算吡啶轴向配合物在各种多重度下的能量(列于表2中), (TPFC)Mn^VO(Py)单重态能量最低, 而(TPFC)Mn^{III}(Py)是五重态的能量最低, 与没有轴向配位的情况是一致的. 在Mn^VO卟啉类化合物的氧转移(OAT)或氢转移(HAT)反应过程中, 三重态下过渡态的能垒低于单重态的, 该体系可能先从单重态激发到三重态, 再发生转移反应.²¹⁻²³ 本文选择配体

表2 吡啶与(TPFC)Mn^VO和(TPFC)Mn^{III}轴向配合物不同电子态下的能量(a.u.)

Table 2 Energies (a.u.) of axial complexes formed by pyridine coordinated with (TPFC)Mn ^{III} or (TPFC)Mn ^V O in different electronic states			
Complex	Energy/(a.u.)		
	singlet	triplet	quintet
(TPFC)Mn ^{III} (Py)	-3483.576	-3483.606	-3483.619
(TPFC)Mn ^V O(Py)	-3558.807	-3558.787	-3558.778

与(TPFC)Mn^{III} (五重态)和(TPFC)Mn^VO (单和三重态)的相互作用为研究对象, 在不加任何对称性限制下进行几何优化计算, 同时进行频率验证, 结果均无虚频, 说明优化的结构为稳定构型. 在优化构型上以同级水平上进行NBO²⁴分析. 通过计算轴向配位的结合能 ΔE ($\Delta E = E_{\text{ML}} - E_{\text{M}} - E_{\text{L}}$, M表示(TPFC)Mn^VO或(TPFC)Mn^{III}, L表示配体), 以反映配体与(TPFC)Mn^VO, (TPFC)Mn^{III}结合的强弱. 所有的计算均采用Gaussian 03程序,²⁵ 在华南师范大学高性能计算平台(曙光5000系列)完成.

3 结果与讨论

3.1 (TPFC)Mn^{III}与配体的轴向配位作用

配体咪唑、4-甲基咪唑和吡啶与五重态下的(TPFC)Mn^{III}配位后优化的几何构型见图2, 几何参数列于表3. 几何结构数据中, (TPFC)Mn^{III}中Mn与大环平面的距离为0.0005 nm, 说明Mn几乎处于corrole大环平面内. 配位后, Mn原子沿轴向偏离大环平面, 偏离的距离在0.0236–0.0279 nm之间, 相应地Mn—N的键长被拉长. $D_{\text{L-NNNN}}$ 表示的是配体所在的平面与corrole的四个N形成平面的夹角, 角度接近90°, 说明配体与corrole大环平面基本垂直. 咪唑形成的配位键长为0.2259 nm, 短于4-甲基咪唑(0.2289 nm)和吡啶的(0.2302 nm). 计算结果显示咪唑与(TPFC)Mn^{III}的结合能绝对值(含零点能校正)为58.643 kJ·mol⁻¹, 比4-甲基咪唑(56.220 kJ·mol⁻¹)和吡

图2 五重态下(TPFC)Mn^{III}(L)(L=Im, 4-MI, Py)的优化构型

Fig.2 Optimization structures of (TPFC)Mn^{III}(L) (L=Im, 4-MI, Py) in the quintet state

啉($49.322 \text{ kJ} \cdot \text{mol}^{-1}$)都大, 配位键的键长与结合能大小的顺序是一致的, 次序为咪唑>4-甲基咪唑>吡啶, B3LYP方法下计算的结果类似(数据见 Supporting Information 中的表 S1), 与实验上得到的配位常数大小顺序¹⁸相符.

表3给出五重态下(TPFC)Mn^{III}(L)和(TPFC)Mn^{III}的原子或基团的自然布居分析(NPA)电荷及配位键的 Wiberg 键级(WI).²⁶发现咪唑与4-甲基咪唑的键级相近, 两者均大于吡啶的 WI, Wiberg 键级越大, 配位键越强. 另外, 配体与(TPFC)Mn^{III}配位后, 咪唑、4-甲基咪唑和吡啶的净电荷分别为 0.119e、0.119e、0.117e, 显示 Wiberg 键级越大, 转移到(TPFC)Mn^{III}的负电荷是最多的.

一般来说, 配位氮原子的电荷越负, 越容易配位. 具有供电子甲基的4-甲基咪唑上的配位 N 原子的负电荷最多, 其结合能及其配位能力应该最强,

表3 五重态下(TPFC)Mn^{III}(L)的优化几何结构参数、结合能(ΔE)、NPA 电荷及配位键的 Wiberg 键级(WI)

Table 3 Selected optimized geometrical parameters, binding energy (ΔE), NPA charge, and Wiberg bond order (WI) of coordination bond of (TPFC)Mn^{III}(L) in the quintet state

Parameter	(TPFC)Mn ^{III} (L)			(TPFC)Mn ^{III}
	Im	4-MI	Py	
$d_{\text{Mn-N}}^a/\text{nm}$	0.1924	0.1927	0.1922	0.1903
$\Delta d(\text{N4})/\text{nm}$	0.0245	0.0279	0.0236	0.0005
$d_{\text{Mn-L}}/\text{nm}$	0.2259	0.2289	0.2302	
	(0.2283) ^b	(0.2316) ^b	(0.2331) ^b	
$D_{\text{L-NNNN}}^c/(\circ)$	89.07	89.40	88.50	
$D_{\text{NNNN}}^d/(\circ)$	2.467	0.346	-0.469	-0.661
$\Delta E^e/(\text{kJ} \cdot \text{mol}^{-1})$	-58.643	-56.220	-49.322	
	(-66.696) ^b	(-64.700) ^b	(-54.975) ^b	
Q_{L}^f/e	0.119	0.119	0.117	
Q_{N}^g/e	-0.477	-0.482	-0.436	
Q_{N}^h/e	-0.561	-0.559	-0.501	
Q_{AN}^i/e	-0.084	-0.077	-0.065	
Q_{Mn}^j/e	1.277	1.234	1.277	1.287
Q_{AN}^k/e	-2.210	-2.216	-2.208	-2.299
Q_{corrole}^l/e	-1.396	-1.353	-1.394	-1.287
WI	0.29	0.29	0.27	

^aaverage bonding lengths of four Mn—N bonds; ^bat B3LYP level, the detail see Supporting Information; ^cdihedral angle between the plane of ligand and the mean plane of the four nitrogen atoms in pyrroles; ^ddihedral angle of four nitrogen atoms in pyrroles; ^ewith zero-point energy correction; ^fafter coordination; ^gbefore coordinating; ^h Q_{L} is the natural charge of ligands; Q_{N} is the natural charge of coordinated N atom; Q_{AN} is the difference natural charge of N atoms before and after coordination; Q_{AN} is the sum natural charge of four pyrroles nitrogen atom; Q_{corrole} is the sum natural charge corrole skeleton. NPA: natural population analysis

观察配体配位氮原子的负电荷绝对值大小顺序: 4-甲基咪唑(0.482e)>咪唑(0.477e)>吡啶(0.436e), 但次序与实验结果获得的配位常数大小顺序¹⁸不一致, 由此可见结合能和配位能力的影响因素不仅有配体的电子效应, 还可能有空间效应.

3.2 配体的空间效应对轴向配位作用的影响

咪唑是五元环的共轭体系, 若环上连有甲基, 会使得配位 N 原子上的电荷密度从-0.477 增至-0.482, 理论上存在供电基的4-甲基咪唑的配位能力会强于未取代的咪唑, 但从实验得到的配位常数¹⁸和计算结果的结合能均表示咪唑配位能力强于4-甲基咪唑. 优化的几何结构显示(图2), 配体上的配位 N 原子与相邻的 C 原子分别与 Mn 原子形成夹角, 左边的夹角为 118.86°和右边的夹角为 134.24°, 而配体为咪唑时左边的夹角和右边的夹角相差不大, 分别为 128.20°和 125.07°, 这是由于4-甲基咪唑的空间位阻, 甲基与大环平面有排斥, 没有甲基一端明显向着大环平面倾斜. 考虑到空间位阻可能显著影响到配位结合能, 因此进一步计算了甲基在咪唑的2-位和5-位取代以及空间位阻更大的异丙基在咪唑的2-位、4-位和5-位时的配位作用情况(结构见图1). 结果(表4)显示2-位与4-位上取代时相互作用相似, 如2-甲基咪唑和4-甲基咪唑的配位结合能绝对值非常接近, 分别为 56.346 和 56.220 $\text{kJ} \cdot \text{mol}^{-1}$. 5-位取代时空间位阻比较小, 因此5-甲基咪唑的配位结合能绝对值增加至 58.475 $\text{kJ} \cdot \text{mol}^{-1}$, 相应增加了约 2 $\text{kJ} \cdot \text{mol}^{-1}$. 上述甲基咪唑的配位结合能均小于咪唑的计算值, 显然空间效应对配位结合能有重要的影响. 咪唑环上引进体积更大的异丙基后, 4-异丙基咪唑的配位 N 原子的电荷为-0.559, 与4-甲基咪唑的一样, 但4-异丙基咪唑的结合能绝对值比4-甲基咪唑的减少了 8.709 $\text{kJ} \cdot \text{mol}^{-1}$, 2-位和5-位取代时也有相似的情况, 以上都说明了配体上取代基的空间位阻会降低配体的结合能力. 所以4-位取代基的空间位阻对配位作用确实存在影响, 使其配位键能下降, 导致空间位阻较大的4-甲基咪唑的配位能力弱于咪唑.

咪唑、4-甲基咪唑、吡啶的结合能大小的顺序与配位键键长长短规律是一致的, 即配位键越短, 结合能力越强. 而表4数据显示5-甲基咪唑的配合能力是最强的, 但配位键的键长不是最短的. 考虑到配位键与大环平面的倾斜角度对配位键的有效成键可能存在影响, 所以在表4给出了配位键与四

表4 五重态下(TPFC)Mn^{III}(L)轴向配位结合能(ΔE), 配体和配位N原子的NPA电荷及其部分几何结构参数
Table 4 Axial binding energy (ΔE), NPA charge for ligands and coordination nitrogen atom, selected optimized geometrical parameters of (TPFC)Mn^{III}(L) in the quintet state

Parameter	2-MI	5-MI	2-IPI	4-IPI	5-IPI
Q_N^a/e	-0.561	-0.556	-0.588	-0.559	-0.552
Q_N^b/e	-0.484	-0.477	-0.492	-0.488	-0.476
Q_L^c/e	0.118	0.124	0.116	0.113	0.123
$\Delta E^d/(kJ \cdot mol^{-1})$	-56.346	-58.475	-51.667	-47.511	-55.267
d_{Mn-L}/nm	0.2277	0.2257	0.2284	0.2304	0.2250
$A_{NMnN1}/(^{\circ})$	96.03	99.28	95.2	101.04	98.36
$A_{NMnN2}/(^{\circ})$	101.17	99.94	101.73	93.94	100.54
$A_{NMnN3}/(^{\circ})$	100.83	96.02	102.39	95.36	96.68
$A_{NMnN4}/(^{\circ})$	95.5	96.67	95.06	103.79	95.93

^aafter coordinating c; ^bbefore coordinating; ^cwith zero-point energy correction; $A_{NMnN(1-4)}$ is the angle between coordination bond and Mn—N bond formed by manganese atom with nitrogen atom from four pyrroles.

个吡咯N原子形成的夹角. 发现小位阻的5-甲基咪唑的四个 A_{NMnN1} 、 A_{NMnN2} 、 A_{NMnN3} 、 A_{NMnN4} 夹角分别为 99.28°、99.94°、96.02°、96.97°, A_{NMnN1} 与 A_{NMnN2} 的角度接近, A_{NMnN3} 与 A_{NMnN4} 也类似, 两类角度差值约 3°, 表明该体系的配位键发生轻微的倾斜. 与其他体系相比, 5-甲基咪唑的角度差值小于 2-甲基咪唑和 4-甲基咪唑的角度差值(约 5°), 更明显小于位阻稍大的 2-异丙基咪唑和 4-异丙基咪唑的角度差值(约 7°), 角度差值越大, 结合能的数值越小, 说明随着配位

键与大环平面的倾斜度增大, 有效成键减少, 结合能降低.

3.3 (TPFC)Mn^{III}(L)的前线轨道分析

(TPFC)Mn^{III}与咪唑配位后的前线分子轨道见图3, 各配体和(TPFC)Mn^{III}配位后的前线分子轨道非常相似, 故本文中仅给出咪唑与(TPFC)Mn^{III}配位后的前线分子轨道. (TPFC)Mn^{III}(Im)和(TPFC)Mn^{III}的前线轨道主要分布在 corrole 骨架和 Mn 原子上. (TPFC)Mn^{III}(Im)和(TPFC)Mn^{III}的最高占据分子轨道(HOMO)与卟啉的 a_{2u} 轨道²⁷很相似, 而 HOMO-1 轨道与卟啉的 a_{1u} 轨道²⁷很相似. (TPFC)Mn^{III}的 HOMO 在 Mn 原子上基本上没有分布, (TPFC)Mn^{III}(Im)的前线轨道 Mn 原子都带有 d 轨道特征, (TPFC)Mn^{III}(Im)的 α -HOMO 轨道中 Mn 的 d_z 与配体上进行配位 N 原子的 p_z 形成一个弱 σ^* 轨道, β -HOMO 轨道的 Mn 具有 d_z 特征. 对于最低空分子轨道(LUMO)来说, (TPFC)Mn^{III}的 α -和 β -LUMO 中 Mn 分别具有 d_{xz} , $d_{x^2-y^2}$ 特征, 与配体轴向配位结合后, α -LUMO 中 Mn 具有 d_{xy} 特征, β -HOMO 中 Mn 的轨道分布没有变化. (TPFC)Mn^{III}与配体结合后, 前线轨道分布的变化主要集中在配体和 Mn 原子上.

3.4 卟咯 Mn^VO 与配体的轴向作用

设定(TPFC)Mn^VO与轴向配体配位键 $d_{Mn-N(L)}$ 的初始值在 0.20 nm 左右, 单重态下几何优化后的该距离拉长到 0.40 nm 左右, 超出配位键的合理键长

图3 五重态下(TPFC)Mn^{III}(Im)和(TPFC)Mn^{III}的前线分子轨道
Fig.3 Frontier molecular orbitals of (TPFC)Mn^{III}(Im) and (TPFC)Mn^{III} in the quintet state
HOMO: the highest occupied molecular orbital; LUMO: the lowest unoccupied molecular orbital

表5 单、三重态下(TPFC)Mn^{VO}(L)的优化结合能(ΔE)和结构数据Table 5 Selected optimized geometrical parameters and binding energy (ΔE) of (TPFC)Mn^{VO}(L) in the singlet and triplet

L	$\Delta E^a/(\text{kJ} \cdot \text{mol}^{-1})$		$d_{\text{Mn}-\text{O}}/\text{nm}$		$d_{\text{Mn}-\text{N}(\text{L})}/\text{nm}$	
	singlet	triplet	singlet	triplet	singlet	triplet
Im	9.820	-7.837	0.1556	0.1601	0.4139	0.2409
4-MI	10.108	3.324	0.1556	0.1599	0.4108	0.2626
Py	10.825	-1.701	0.1556	0.1600	0.3640	0.2500

^awith zero-point energy correction; ^bdistance of manganese atom and nitrogen atom of ligands

范围(一般 Mn—N 配位键长在 0.23 nm 左右²⁸). 计算出的结合能列于表 5, 可见基态(单重态)下的(TPFC)Mn^{VO} 与配体不能形成有效的轴向配位键, 这与文献报导 corrole Mn^{VO} 中的 Mn 不能与苯甲硫醚形成配位的结果²¹相似. 三重态下(TPFC)Mn^{VO} 与配体的作用情况见表 5. 三重态(TPFC)Mn^{VO} 的 Mn 原子与配体存在弱的配位作用, 当配体为咪唑时, 与(TPFC)Mn^{VO} 作用最大, 结合能为 $-7.837 \text{ kJ} \cdot \text{mol}^{-1}$, Mn 与配体的 N 原子的距离最短, 为 0.2409 nm. 由于 Mn 原子与配体的作用, 削弱了 Mn 与 O 之间的键强度, $d_{\text{Mn}-\text{O}}$ 从作用前的 0.1599 nm 增加至作用后的 0.1601 nm (图 4), 而吡啶与(TPFC)Mn^{VO} 作用较弱, Mn—O 的距离变化不明显. 三重态(TPFC)Mn^{VO} 与配体的弱作用可用自然键轨道(NBO)分析的二级微扰稳定化能 $E(2)$ ²⁴ 来分析. 表 6 列出了配体咪唑、4-甲基咪唑、吡啶与三重态下的(TPFC)Mn^{VO} 形成弱相互作用主要的二级微扰稳定化能. $E(2)$ 值分别为配体的 N 原子的孤对电子到 Mn 与氧形成的反键轨道的作用($\text{LP}(\text{N}) \rightarrow \sigma^*(\text{Mn}-\text{O})$)和配体的 N 原子的孤对电子到 Mn 的空的孤对轨道的作用($\text{LP}(\text{N}) \rightarrow \text{LP}^*(\text{Mn})$), α 轨道的 $E(2)$ 值大小次序为 $\text{Im} > \text{Py} > 4\text{-MI}$, β 轨道 $E(2)$ 值大小次序与 α 轨道的是相同的. $E(2)$ 值越大, 体系的稳定性越高, 咪唑的 $E(2)$ 值明显大于其它两个配体, 所以咪唑与三重态下(TPFC)Mn^{VO} 形

表6 三重态下(TPFC)Mn^{VO}(L)的二级微扰稳定化能($E(2)$)Table 6 Second order perturbation stabilization energy ($E(2)$) of (TPFC)Mn^{VO}(L) in the triplet

Ligand	Orbital	Doner NBO	Acceptor NBO	$E(2)$ ($\text{kJ} \cdot \text{mol}^{-1}$)
Im	α	LP(N) ^a	LP*(Mn, 4s)	28.075
		LP(N)	$\sigma^*(\text{Mn}-\text{O})^b$	54.936
	β	LP(N)	$\sigma^*(\text{Mn}-\text{O})$	59.455
		LP(N)	LP*(Mn, 4s)	13.431
4-MI	α	LP(N)	LP*(Mn, 4s)	25.481
		LP(N)	$\sigma^*(\text{Mn}-\text{O})$	27.865
	β	LP(N)	$\sigma^*(\text{Mn}-\text{O})$	19.665
		LP(N)	LP*(Mn, 4s)	40.752
Py	α	LP(N)	LP*(Mn, 4s)	43.514
		LP(N)	$\sigma^*(\text{Mn}-\text{O})$	
	β	LP(N)	$\sigma^*(\text{Mn}-\text{O})$	
		LP(N)	LP*(Mn, 4s)	

^aN atom is coordinated atom of ligands; ^b σ^* formed by d_z^2 of Manganese and p_z of nitrogen atom of ligands.

成的 ΔE 值也是最大的, 形成弱的相互作用.

Corrole Mn^{VO} 是一个五配位结构, 其中心金属 Mn 呈 16 电子结构, 理论上还可以再与一个配体形成 18 电子稳定的六配位结构, 但计算结果表明, 单重态下 corrole Mn^{VO} 不能再进行配位, 文献²¹认为 corrole Mn^{VO} 不能配位的原因是金属 Mn 和 corrole 大环有强的 $d-\pi$ 共轭作用, 导致了金属 Mn 形成 18 电子的结构, 达到配位饱和. 我们的轨道分析发现单重态下(TPFC)Mn^{VO} 的电子组态为 $\sigma_z^2 \sigma_{xy}^2 \pi_{xz}^2 \pi_{yz}^2 \delta_{x^2-y^2}^2$, 三重态下的电子组态为 $\sigma_z^2 \sigma_{xy}^2 \pi_{xz}^2 \pi_{yz}^2 \delta_{x^2-y^2}^2 \pi_{xz}^{*1}$, 单、三重态下的 $d_{x^2-y^2}$ 均为非键轨道, 不参与成键, 其它的 d 轨道都参与成键. NBO 计算结果也显示(见图 5)基态的(TPFC)Mn^{VO} 中金属 Mn 的 $d_{x^2-y^2}$ 不参与成键, 为非键轨道, 而 d_{xy} 与 corrole 上四个吡咯的 N 原子形成四个 σ 键轨道, d_{z^2} 、 d_{xz} 和 d_{yz} 分别与轴向的氧原子形成一个 σ 键轨道和两个 π 键轨道, 所以没有空的 3d 轨道接受轴向配体的孤对电子形成配位键. 三重态下的(TPFC)Mn^{VO} 中 Mn 的 $d_{x^2-y^2}$ 和 d_{xy} 的成键与单重态下的情况一致. β 轨道中 Mn 的 d_{z^2} 、 d_{xz} 和 d_{yz} 分别与 O 的 p_z 、 p_x 、 p_y 形成一个 σ 键轨道和两个 π 键轨道. 但体系的 α 轨道中 Mn 的 d_{z^2} 和 d_{xz} 分别与 O 的 p_z 和 p_x 形成一个 σ

图4 单、三重态下(TPFC)Mn^{VO}及(TPFC)Mn^{VO}(Im)优化的几何结构Fig.4 Optimized geometries of (TPFC)Mn^{VO} and (TPFC)Mn^{VO}(Im) in the singlet and triplet

图5 单重态下(TPFC) $\text{Mn}^{\text{V}}\text{O}$ 中Mn参与成键的自然键轨道图Fig.5 Natural bond orbitals of metal Mn atom in (TPFC) $\text{Mn}^{\text{V}}\text{O}$ in the singlet

成键轨道和一个 π 成键轨道. 相比于单重态, 由于三重态的 α 轨道中少了一个 π 成键轨道, 所以三重态下体系的Mn—O键的强度降低, 表现Mn与O的键长从0.1556 nm增至0.1599 nm (图4). 计算结果进一步发现在三重态下(TPFC) $\text{Mn}^{\text{V}}\text{O}$ 可以与配体在轴向方向形成弱的配位作用, 因为配体的N的孤对电子轨道与Mn的空的4s轨道或者与 $\sigma^*(\text{Mn}-\text{O})$ 轨道发生重叠作用(表6), 配体为咪唑时, Mn与配位的N原子距离最短, 配位作用较强.

上述结果说明含氮配体与单重态或三重态下的(TPFC) $\text{Mn}^{\text{V}}\text{O}$ 均难以形成强的配位键, 配体与基态(TPFC) $\text{Mn}^{\text{V}}\text{O}$ 的配位作用不是促进其降解的主要原因. 配体能加快(TPFC) $\text{Mn}^{\text{V}}\text{O}$ 的分解可能是由于配体在(TPFC) $\text{Mn}^{\text{V}}\text{O}$ 降解反应的过渡态阶段参与轴向配位促进其分解, 但是这有待更深入的研究.

4 结 论

采用DFT方法对咪唑、吡啶及甲基/异丙基取代咪唑分别与咪唑锰(V)-氧和咪唑锰(III)配合物的轴向配位作用进行理论计算研究. 计算结果显示, 配体可以咪唑锰(III)配合物进行配位结合, 且配体与咪唑锰(III)配合物的结合能绝对值大小顺序为咪唑($58.643 \text{ kJ} \cdot \text{mol}^{-1}$)>4-甲基咪唑($56.220 \text{ kJ} \cdot \text{mol}^{-1}$)>吡啶($49.322 \text{ kJ} \cdot \text{mol}^{-1}$), 这与实验获得的配位常数顺序一致. 考察单取代咪唑与咪唑锰(III)配位能力的差异, 发现4-甲基咪唑的配位能力弱于咪唑的原因是4位取代基的空间位阻对配位能力存在重要影响, 导致其配位键能小于咪唑的. 配体不能与单、三重态下的咪唑锰(V)-氧配合物的Mn形成有效的轴向

配位结合, 但可与三重态下咪唑锰(V)-氧配合物形成弱配位作用. NBO分析显示单重态咪唑锰(V)-氧配合物的Mn不能与配体进行配位的原因是金属Mn没有多余的空的3d轨道来接受配体的电子, 即单、三重态下的咪唑锰(V)-氧的锰不能再进行有效配位结合.

Supporting Information: available free of charge via the internet at <http://www.whxb.pku.edu.cn>.

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卟咯锰(III)与锰(V)-氧配合物与含氮配体的轴向配位性质

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Axial Coordination Behavior of Corrole Mn^{III} and Mn^VO Complexes with N-Based Ligands

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表 S1 在 B3LYP 方法下五重态(TPFC)Mn^{III}(L)的优化几何结构参数、结合能(ΔE)、NPA 电荷及配位键的 Wiberg 键级(WI)

Table S1 Selected optimized geometrical parameters, binding energy (ΔE), NPA charge and wiberg bond order (WI) of coordination bond of (TPFC)Mn^{III}(L) in the quintet state at B3LYP

	level			
	(TPFC)Mn ^{III} (L)			(TPFC)Mn ^{III}
	Im	4-MI	Py	
$d_{\text{Mn-N}}^{\text{a}}/\text{nm}$	0.1924	0.1928	0.1923	0.1903
$\Delta d(\text{N4})^{\text{b}}/\text{nm}$	0.0256	0.0274	0.0246	0.0005
$d_{\text{Mn-L}}^{\text{c}}/\text{nm}$	0.2283	0.2316	0.2331	
$D_{\text{L-NNNN}}^{\text{d}}/(^{\circ})$	89.23	89.12	88.77	
$D_{\text{NNNN}}^{\text{e}}/(^{\circ})$	-2.162	-0.487	0.438	0.672
$\Delta E^{\text{f}}/(\text{kJ}\cdot\text{mol}^{-1})$	-66.696	-64.700	-54.975	
Q_{L}^{g}	0.101	0.096	0.094	
Q_{N}^{h}	-0.494	-0.501	-0.452	
Q_{N}^{g}	-0.589	-0.593	-0.534	
$Q_{\Delta\text{N}}$	-0.095	-0.092	-0.082	
Q_{Mn}	1.418	1.444	1.417	1.455
$Q_{4\text{N}}$	-2.406	-2.412	-2.422	-2.520
Q_{Corrole}	-1.519	-1.540	-1.511	-1.455
WI	0.29	0.29	0.27	

^a average bonding lengthes of four Mn-N bonds; ^b distances of coordination bond between ligands with (TPFC)Mn^{III}; ^c distances between Mn atom and the mean plane of the four nitrogen atoms in pyrrole; ^d dihedral angle between the plane of ligand and the mean plane of the four nitrogen atoms in pyrrole; ^e dihedral angle of four nitrogen atoms in pyrrole; ^f after zero-point energy correction; ^g after coordination; ^h before coordinating; Q_{L} is the natural charge of ligands; Q_{N} is the natural charge of coordinating N atom; $Q_{\Delta\text{N}}$ is the difference natural charge between Q_{N}^{g} and Q_{N}^{h} ; $Q_{4\text{N}}$ is the sum natural charge of four pyrrole nitrogen atom; Q_{Corrole} is the sum natural charge corrole skeleton.

表 S2 五重态的(TPFC)Mn^{III}(L)在 BP86 方法下优化的部分几何参数

Table S2 Selected optimized parameters of (TPFC)Mn^{III}(L) in the quintet state at BP86 level

Parameter	2-MI	5-MI	4-IPI	2-IPI	5-IPI
$d_{\text{Mn-N1}}/\text{nm}$	0.1922	0.1921	0.1923	0.1922	0.1922
$d_{\text{Mn-N2}}/\text{nm}$	0.1923	0.1921	0.1924	0.1924	0.1922
$d_{\text{Mn-N3}}/\text{nm}$	0.1933	0.1932	0.1935	0.1936	0.1931
$d_{\text{Mn-N4}}/\text{nm}$	0.1934	0.1933	0.1935	0.1932	0.1934
$d_{\text{Mn-N}}^{\text{a}}/\text{nm}$	0.1928	0.1927	0.1929	0.1929	0.1927
$d_{\text{Mn-L}}^{\text{b}}/\text{nm}$	0.2277	0.2257	0.2284	0.2304	0.2251
$\Delta d(\text{N4})^{\text{c}}/\text{nm}$	0.0281	0.0264	0.0289	0.0289	0.0261
$D_{\text{NNNN}}^{\text{d}}/(\text{°})$	-0.435	-0.922	-0.117	-0.121	-1.186

^a average bonding lengths of four Mn-N bonds; ^b distances of coordination bond between ligands with (TPFC)Mn^{III};

^c distances between Mn atom and the mean plane of the four nitrogen atoms in pyrrole; ^d dihedral angle of four nitrogen atoms in pyrroles

图 S1 五重态下(TPFC)Mn^{III}(L)和(TPFC)Mn^{III}的前线分子轨道的分布图(BP86 方法)

Fig.S1 Frontier molecular orbitals of (TPFC)Mn^{III}(L) and (TPFC)Mn^{III} in the quintet at BP86 level

表 S3 在 B3LYP 方法下单、三重态 (TPFC)Mn^VO(L)的结合能(ΔE)和结构数据

Table S3 Selected optimized geometrical parameters and binding energy (ΔE) of (TPFC)Mn^VO(L) in the singlet and triplet at B3LYP level

L	$\Delta E^a/(\text{kJ}\cdot\text{mol}^{-1})$		$d_{\text{Mn-O}}/\text{nm}$		$d_{\text{Mn-N(L)}}/\text{nm}$	
	Singlet	Triplet	Singlet	Triplet	Singlet	Triplet
Im	5.122	-8.457	0.1535	0.158	0.3945	0.2499
4-MI	3.166	0.055	0.1535	0.1575	0.4104	0.2973
Py	5.821	-0.751	0.1535	0.1578	0.3913	0.2678

^a with zero-point energy correction; ^b distance of manganese atom and nitrogen atom of ligand.

Cartesian Coordinates of Optimized Geometries

(TPFC)Mn^{III}(Im)

1	25	0	-0.019707	-0.924280	-0.151391
2	7	0	-1.273554	-2.342160	-0.447183
3	7	0	1.423865	0.344808	-0.308137
4	7	0	1.202425	-2.347235	-0.563603
5	9	0	-4.767054	-2.413258	1.866792
6	7	0	-1.455107	0.358601	-0.289086
7	9	0	-5.216765	-0.247735	-2.367957
8	9	0	-7.468539	-2.708811	1.992596
9	9	0	-7.917527	-0.521704	-2.211368
10	9	0	-9.055910	-1.759705	-0.039746
11	9	0	4.966928	-2.152880	-2.688546
12	9	0	9.010745	-1.740835	-0.254713
13	9	0	-0.912954	4.079625	-2.346802
14	9	0	7.669545	-2.409503	-2.557163
15	9	0	-0.896210	6.795110	-2.208685
16	9	0	7.618241	-0.828833	1.932678
17	9	0	0.047938	8.056126	0.042459
18	9	0	0.927481	3.857986	2.054509
19	9	0	4.913345	-0.598350	1.831866
20	6	0	2.555839	2.336031	-0.366100
21	1	0	2.743816	3.408686	-0.397386
22	6	0	-2.646318	-2.386078	-0.459473
23	9	0	0.964410	6.574401	2.167316
24	6	0	4.842872	-1.359976	-0.438072
25	6	0	-3.026443	-3.760705	-0.662589
26	1	0	-4.049894	-4.129124	-0.734407
27	6	0	-4.896762	-1.323715	-0.258498

28	6	0	0.034455	6.712951	-0.019930
29	6	0	-5.516844	-1.952728	0.840303
30	6	0	-1.268494	1.733281	-0.212366
31	6	0	5.589233	-1.829555	-1.537945
32	6	0	-2.828339	0.093465	-0.254116
33	6	0	-3.413823	-1.196611	-0.326398
34	6	0	0.006043	3.871931	-0.151231
35	6	0	-5.741854	-0.846721	-1.281059
36	6	0	6.985465	-1.964655	-1.486637
37	6	0	6.961140	-1.148197	0.800864
38	6	0	-0.759273	-3.614754	-0.652358
39	6	0	5.566188	-1.030533	0.726384
40	6	0	-0.004637	2.379482	-0.218644
41	6	0	-1.856519	-4.518156	-0.782657
42	1	0	-1.789261	-5.591793	-0.958298
43	6	0	-2.566343	2.356519	-0.118266
44	1	0	-2.743741	3.428275	-0.037230
45	6	0	0.667058	-3.620302	-0.695959
46	6	0	-7.137187	-0.983378	-1.216125
47	6	0	-6.907890	-2.108935	0.924743
48	6	0	-3.516425	1.354951	-0.138367
49	1	0	-4.597716	1.475379	-0.081848
50	6	0	7.673291	-1.619436	-0.313166
51	6	0	-7.720639	-1.620000	-0.109871
52	6	0	0.505789	5.954332	1.062516
53	6	0	3.359405	-1.233200	-0.479792
54	6	0	-0.455419	4.664426	-1.222061
55	6	0	-0.451073	6.066783	-1.167144
56	6	0	1.748572	-4.544002	-0.818806
57	1	0	1.662449	-5.623056	-0.946739
58	6	0	3.494802	1.323784	-0.419116
59	1	0	4.575483	1.434302	-0.505244
60	6	0	2.791765	0.065742	-0.392907
61	6	0	0.482327	4.553619	0.986850
62	6	0	2.574726	-2.413835	-0.589705
63	6	0	2.931226	-3.801275	-0.746258
64	1	0	3.946938	-4.191940	-0.806707
65	6	0	1.252419	1.723365	-0.291234
66	6	0	1.192651	-0.956844	2.827470
67	6	0	-0.944589	-1.369143	2.986814
68	6	0	-0.446859	-1.402026	4.272857
69	7	0	0.910784	-1.139349	4.150389
70	1	0	1.582129	-1.086123	4.912727
71	1	0	2.187631	-0.743174	2.440442

72	1	0	-1.963200	-1.530235	2.639144
73	1	0	-0.916978	-1.581754	5.236028
74	7	0	0.083693	-1.090738	2.099541

(TPFC)Mn^{III}(4-MI)

1	25	0	-0.011900	-0.914117	-0.090304
2	7	0	-1.262250	-2.323920	-0.473187
3	7	0	1.437922	0.347829	-0.266508
4	7	0	1.217258	-2.345493	-0.453804
5	9	0	-4.868777	-2.423307	1.631819
6	7	0	-1.438678	0.375048	-0.305211
7	9	0	-5.097531	-0.166520	-2.575398
8	9	0	-7.571753	-2.706894	1.615879
9	9	0	-7.803160	-0.429935	-2.558035
10	9	0	-9.053431	-1.707357	-0.472749
11	9	0	4.995350	-0.262797	-2.659117
12	9	0	9.016306	-1.821812	-0.698392
13	9	0	-0.748054	4.183945	-2.235539
14	9	0	7.696868	-0.552060	-2.745588
15	9	0	-0.717800	6.891866	-1.978366
16	9	0	7.609202	-2.789197	1.454936
17	9	0	0.094125	8.043719	0.379850
18	9	0	0.817809	3.752841	2.254716
19	9	0	4.909376	-2.480384	1.571380
20	6	0	2.575097	2.338351	-0.215558
21	1	0	2.764817	3.410724	-0.185860
22	6	0	-2.632479	-2.359010	-0.573098
23	9	0	0.866103	6.462933	2.489896
24	6	0	4.856561	-1.360946	-0.540596
25	6	0	-3.007724	-3.726138	-0.828180
26	1	0	-4.026851	-4.085542	-0.971625
27	6	0	-4.885614	-1.287913	-0.476335
28	6	0	0.074467	6.704803	0.257824
29	6	0	-5.563844	-1.936895	0.575239
30	6	0	-1.250370	1.746590	-0.189757
31	6	0	5.610673	-0.877351	-1.629270
32	6	0	-2.812892	0.118423	-0.344128
33	6	0	-3.401029	-1.166701	-0.465827
34	6	0	0.031763	3.873711	0.000853
35	6	0	-5.677702	-0.785372	-1.528943
36	6	0	7.005317	-1.021876	-1.690259
37	6	0	6.960152	-2.172496	0.448793
38	6	0	-0.744797	-3.595146	-0.679868
39	6	0	5.567901	-2.008559	0.490033

40	6	0	0.014673	2.384940	-0.127855
41	6	0	-1.836565	-4.488023	-0.896527
42	1	0	-1.763869	-5.557188	-1.095821
43	6	0	-2.547837	2.376240	-0.145772
44	1	0	-2.723133	3.447517	-0.054411
45	6	0	0.681121	-3.606698	-0.669064
46	6	0	-7.075259	-0.916325	-1.535752
47	6	0	-6.957412	-2.088151	0.588957
48	6	0	-3.500448	1.381402	-0.237013
49	1	0	-4.582650	1.507340	-0.236348
50	6	0	7.680950	-1.674832	-0.647810
51	6	0	-7.715986	-1.573282	-0.473891
52	6	0	0.471988	5.895553	1.333290
53	6	0	3.374180	-1.222119	-0.475368
54	6	0	-0.355873	4.715572	-1.060945
55	6	0	-0.343623	6.114284	-0.944590
56	6	0	1.759224	-4.517496	-0.883972
57	1	0	1.669490	-5.584943	-1.085265
58	6	0	3.512311	1.327542	-0.307151
59	1	0	4.594996	1.439469	-0.351533
60	6	0	2.807253	0.072191	-0.354049
61	6	0	0.443164	4.499785	1.194490
62	6	0	2.586474	-2.401574	-0.555911
63	6	0	2.940787	-3.774251	-0.813364
64	1	0	3.954635	-4.148847	-0.954334
65	6	0	1.269912	1.725558	-0.192772
66	6	0	-1.379557	-1.495284	2.696500
67	6	0	0.635206	-0.834599	3.259324
68	6	0	-0.044629	-1.105147	4.433113
69	7	0	-1.314900	-1.519893	4.056583
70	1	0	-2.067898	-1.796625	4.681394
71	7	0	-0.216975	-1.085568	2.183468
72	1	0	0.258266	-1.040060	5.475062
73	1	0	-2.268014	-1.769410	2.130112
74	6	0	2.040570	-0.347035	3.089005
75	1	0	2.644802	-1.052450	2.494424
76	1	0	2.063733	0.626541	2.570880
77	1	0	2.524210	-0.225350	4.071119
(TPFC)Mn ^{III} (Py)					
1	25	0	0.005952	-0.923904	-0.165725
2	7	0	1.251158	-2.352760	-0.451996
3	7	0	-1.436253	0.340166	-0.347457
4	7	0	-1.227188	-2.358972	-0.474306

5	9	0	5.038766	-2.110685	-2.571157
6	7	0	1.442448	0.347596	-0.343661
7	9	0	4.910004	-0.586419	1.953868
8	9	0	7.743170	-2.349447	-2.404957
9	9	0	7.618665	-0.800914	2.094594
10	9	0	9.046545	-1.688069	-0.079095
11	9	0	-4.953449	-0.566323	1.840485
12	9	0	-9.033729	-1.724436	-0.273161
13	9	0	-0.840226	3.956048	1.873705
14	9	0	-7.663919	-0.788419	1.917610
15	9	0	-0.872040	6.675954	1.863243
16	9	0	-7.670063	-2.426278	-2.551944
17	9	0	-0.041953	8.055857	-0.363249
18	9	0	0.820600	3.970585	-2.602634
19	9	0	-4.963608	-2.179417	-2.655739
20	6	0	-2.562959	2.332630	-0.464831
21	1	0	-2.747775	3.404296	-0.529582
22	6	0	2.624514	-2.406497	-0.462441
23	9	0	0.809352	6.690476	-2.590262
24	6	0	-4.865370	-1.356024	-0.415256
25	6	0	2.995701	-3.794016	-0.572015
26	1	0	4.016062	-4.175526	-0.607160
27	6	0	4.881700	-1.331954	-0.318478
28	6	0	-0.031590	6.711380	-0.363830
29	6	0	5.644856	-1.789051	-1.411399
30	6	0	1.261241	1.725799	-0.350737
31	6	0	-5.598475	-1.009811	0.737840
32	6	0	2.816024	0.078694	-0.352144
33	6	0	3.396987	-1.215830	-0.383905
34	6	0	-0.008805	3.868320	-0.364642
35	6	0	5.584198	-1.006667	0.859204
36	6	0	-6.994769	-1.123715	0.797979
37	6	0	-6.996382	-1.968873	-1.480045
38	6	0	0.729478	-3.634565	-0.563474
39	6	0	-5.599358	-1.838177	-1.517502
40	6	0	-0.001512	2.373817	-0.362012
41	6	0	1.821056	-4.550462	-0.639595
42	1	0	1.747207	-5.633412	-0.738515
43	6	0	2.562953	2.347199	-0.350826
44	1	0	2.745619	3.421114	-0.352886
45	6	0	-0.696984	-3.638359	-0.573390
46	6	0	6.979005	-1.116547	0.952169
47	6	0	7.041113	-1.915523	-1.341600
48	6	0	3.510038	1.341898	-0.351287

49	1	0	4.593086	1.459755	-0.372153
50	6	0	-7.695484	-1.607038	-0.318201
51	6	0	7.709390	-1.574690	-0.155547
52	6	0	0.406504	6.012100	-1.499024
53	6	0	-3.380409	-1.233928	-0.445224
54	6	0	-0.438451	4.601874	0.759416
55	6	0	-0.458519	6.004740	0.771072
56	6	0	-1.782328	-4.560798	-0.659428
57	1	0	-1.701065	-5.643737	-0.752530
58	6	0	-3.505411	1.322844	-0.473695
59	1	0	-4.586704	1.433842	-0.549973
60	6	0	-2.806804	0.063963	-0.409660
61	6	0	0.408445	4.608721	-1.489024
62	6	0	-2.600112	-2.420781	-0.501571
63	6	0	-2.961947	-3.810947	-0.609517
64	1	0	-3.979552	-4.198625	-0.654930
65	6	0	-1.260488	1.718462	-0.383654
66	6	0	-1.175492	-1.001402	2.818489
67	6	0	-1.229758	-1.047783	4.217608
68	6	0	-0.027696	-1.075150	4.939894
69	6	0	1.184706	-1.054906	4.234848
70	6	0	1.150596	-1.008631	2.835044
71	7	0	-0.007441	-0.982631	2.135745
72	1	0	-0.035659	-1.109956	6.034063
73	1	0	-2.089291	-0.973345	2.215398
74	1	0	-2.199140	-1.059617	4.723801
75	1	0	2.146718	-1.072693	4.754757
76	1	0	2.073153	-0.986829	2.245185

(TPFC)Mn^{III}(2-MI)

1	25	0	-0.023115	-0.926418	-0.062837
2	7	0	-1.273383	-2.343423	-0.411455
3	7	0	1.425899	0.334658	-0.274242
4	7	0	1.206579	-2.361699	-0.415740
5	9	0	-4.907663	-2.454979	1.644026
6	7	0	-1.451228	0.358344	-0.289672
7	9	0	-5.081629	-0.177129	-2.553511
8	9	0	-7.611380	-2.731349	1.595624
9	9	0	-7.787438	-0.433680	-2.569326
10	9	0	-9.065449	-1.717510	-0.504636
11	9	0	4.956198	-0.350283	-2.715770
12	9	0	9.002305	-1.830650	-0.745096
13	9	0	-0.821845	4.162702	-2.237828
14	9	0	7.657918	-0.637497	-2.821693

15	9	0	-0.787088	6.870698	-1.991659
16	9	0	7.621056	-2.721988	1.457622
17	9	0	0.090563	8.032929	0.337907
18	9	0	0.869322	3.750451	2.209847
19	9	0	4.921092	-2.413195	1.592468
20	6	0	2.560540	2.327339	-0.267769
21	1	0	2.749339	3.400289	-0.258557
22	6	0	-2.643155	-2.379324	-0.514981
23	9	0	0.923358	6.460408	2.431596
24	6	0	4.843440	-1.373746	-0.559268
25	6	0	-3.017951	-3.749374	-0.755548
26	1	0	-4.036985	-4.110202	-0.895408
27	6	0	-4.897179	-1.306873	-0.455372
28	6	0	0.068006	6.693553	0.221840
29	6	0	-5.588435	-1.960701	0.585253
30	6	0	-1.264160	1.730896	-0.188037
31	6	0	5.584325	-0.927200	-1.672399
32	6	0	-2.825317	0.099645	-0.320719
33	6	0	-3.412805	-1.186786	-0.428917
34	6	0	0.019280	3.860472	-0.022514
35	6	0	-5.675519	-0.798354	-1.515552
36	6	0	6.978720	-1.071111	-1.743242
37	6	0	6.959635	-2.144296	0.436274
38	6	0	-0.755987	-3.616424	-0.604486
39	6	0	5.567674	-1.981618	0.485953
40	6	0	0.000985	2.371490	-0.142984
41	6	0	-1.847444	-4.512175	-0.812051
42	1	0	-1.774324	-5.583708	-0.997828
43	6	0	-2.562215	2.359305	-0.142483
44	1	0	-2.738945	3.430891	-0.058148
45	6	0	0.669850	-3.626942	-0.604000
46	6	0	-7.072935	-0.926077	-1.540017
47	6	0	-6.982874	-2.108262	0.580198
48	6	0	-3.513727	1.362644	-0.222539
49	1	0	-4.596032	1.486909	-0.216445
50	6	0	7.667193	-1.685027	-0.685523
51	6	0	-7.727577	-1.586398	-0.488867
52	6	0	0.496492	5.888599	1.288615
53	6	0	3.361392	-1.236308	-0.482023
54	6	0	-0.398183	4.698444	-1.076275
55	6	0	-0.383792	6.097648	-0.965603
56	6	0	1.746783	-4.540371	-0.813811
57	1	0	1.656034	-5.611200	-0.995786
58	6	0	3.498112	1.316272	-0.360896

59	1	0	4.579757	1.429278	-0.426031
60	6	0	2.794222	0.059626	-0.378869
61	6	0	0.464088	4.492567	1.155931
62	6	0	2.574765	-2.418322	-0.531251
63	6	0	2.928312	-3.795045	-0.767688
64	1	0	3.941118	-4.171129	-0.912609
65	6	0	1.256709	1.713297	-0.216893
66	6	0	0.695212	-0.713096	3.176232
67	6	0	-1.350965	-1.425884	2.832113
68	6	0	-1.196120	-1.359356	4.198526
69	7	0	0.101709	-0.908008	4.395581
70	1	0	0.547823	-0.743807	5.294849
71	1	0	-2.224292	-1.731364	2.259539
72	7	0	-0.176772	-1.025113	2.207056
73	1	0	-1.865151	-1.585362	5.024362
74	6	0	2.097210	-0.218185	3.016997
75	1	0	2.576178	-0.084803	4.000421
76	1	0	2.705534	-0.926455	2.431650
77	1	0	2.114682	0.750195	2.489956

(TPFC)Mn^{III}(5-MI)

1	25	0	0.001196	-0.901076	-0.108290
2	7	0	-1.244719	-2.325883	-0.434643
3	7	0	1.444010	0.369788	-0.296658
4	7	0	1.235566	-2.330745	-0.460474
5	9	0	-4.971520	-2.497398	1.498967
6	7	0	-1.431878	0.380364	-0.313981
7	9	0	-4.967345	-0.108389	-2.639624
8	9	0	-7.670303	-2.761239	1.333321
9	9	0	-7.669209	-0.352101	-2.771730
10	9	0	-9.035102	-1.684436	-0.795190
11	9	0	4.927971	-0.173956	-2.723464
12	9	0	9.022916	-1.746787	-0.936827
13	9	0	-0.727220	4.253452	-2.197708
14	9	0	7.625369	-0.438401	-2.907205
15	9	0	-0.706401	6.953020	-1.863360
16	9	0	7.695567	-2.778455	1.237039
17	9	0	0.067351	8.039580	0.537506
18	9	0	0.773148	3.700850	2.305089
19	9	0	5.001535	-2.494130	1.452792
20	6	0	2.574621	2.363324	-0.222265
21	1	0	2.760823	3.436074	-0.180829
22	6	0	-2.613252	-2.361768	-0.558849
23	9	0	0.810286	6.400389	2.614785

24	6	0	4.866514	-1.320235	-0.625770
25	6	0	-2.981909	-3.727434	-0.828646
26	1	0	-3.998486	-4.087739	-0.986212
27	6	0	-4.869881	-1.290033	-0.562889
28	6	0	0.052890	6.704938	0.377213
29	6	0	-5.604967	-1.970801	0.430061
30	6	0	-1.252071	1.752010	-0.193280
31	6	0	5.581153	-0.806023	-1.727825
32	6	0	-2.805061	0.114903	-0.355091
33	6	0	-3.387159	-1.171999	-0.480440
34	6	0	0.021889	3.880826	0.038645
35	6	0	-5.603835	-0.752360	-1.641089
36	6	0	6.973628	-0.938134	-1.839953
37	6	0	7.008399	-2.140974	0.269336
38	6	0	-0.721967	-3.593637	-0.653560
39	6	0	5.616989	-1.988944	0.363518
40	6	0	0.011535	2.395823	-0.126025
41	6	0	-1.809409	-4.487717	-0.886560
42	1	0	-1.732330	-5.555004	-1.094232
43	6	0	-2.552897	2.374222	-0.146852
44	1	0	-2.735411	3.444010	-0.051031
45	6	0	0.704960	-3.596638	-0.662706
46	6	0	-6.999198	-0.873660	-1.726516
47	6	0	-6.998895	-2.112178	0.362161
48	6	0	-3.499110	1.373752	-0.247241
49	1	0	-4.582018	1.492905	-0.245134
50	6	0	7.688838	-1.611016	-0.837529
51	6	0	-7.698377	-1.558927	-0.721172
52	6	0	0.435867	5.866563	1.435650
53	6	0	3.385772	-1.192542	-0.516370
54	6	0	-0.352850	4.751948	-1.004019
55	6	0	-0.345603	6.147167	-0.847350
56	6	0	1.785659	-4.499882	-0.894152
57	1	0	1.700769	-5.568573	-1.091192
58	6	0	3.514678	1.356662	-0.327313
59	1	0	4.597036	1.472563	-0.370354
60	6	0	2.814328	0.098513	-0.383096
61	6	0	0.411540	4.476546	1.253811
62	6	0	2.603500	-2.376812	-0.584982
63	6	0	2.962793	-3.747099	-0.846588
64	1	0	3.976702	-4.115295	-1.002907
65	6	0	1.271689	1.744837	-0.205717
66	6	0	0.221469	0.115471	2.944160
67	6	0	-0.229380	-2.015087	2.979353

68	6	0	-0.154518	-1.628625	4.304859
69	7	0	0.133043	-0.265791	4.253229
70	1	0	0.258942	0.346328	5.056315
71	7	0	0.004719	-0.930628	2.148112
72	1	0	0.433140	1.133580	2.621995
73	1	0	-0.438079	-3.002288	2.571671
74	6	0	-0.320056	-2.383754	5.585617
75	1	0	0.596869	-2.363413	6.201973
76	1	0	-1.147198	-1.984008	6.199596
77	1	0	-0.549135	-3.437312	5.365741

(TPFC)Mn^{III}(2-IPi)

1	25	0	-0.099547	-0.901874	-0.126534
2	7	0	-1.338986	-2.323624	-0.498565
3	7	0	1.334495	0.379721	-0.341258
4	7	0	1.144775	-2.316424	-0.517232
5	9	0	-4.994587	-2.424266	1.582301
6	7	0	-1.543515	0.371070	-0.326350
7	9	0	-5.143139	-0.227113	-2.656514
8	9	0	-7.698582	-2.719431	1.515058
9	9	0	-7.848569	-0.501314	-2.694000
10	9	0	-9.137884	-1.754653	-0.618054
11	9	0	4.723722	-0.143348	-2.921230
12	9	0	8.903697	-1.664018	-1.293705
13	9	0	-0.890255	4.179242	-2.286244
14	9	0	7.413570	-0.384696	-3.214039
15	9	0	-0.885360	6.888696	-2.042872
16	9	0	7.676570	-2.690009	0.941894
17	9	0	-0.088095	8.059781	0.310829
18	9	0	0.669379	3.786551	2.210966
19	9	0	4.991115	-2.431096	1.265731
20	6	0	2.442452	2.388463	-0.345805
21	1	0	2.616254	3.463803	-0.326028
22	6	0	-2.708378	-2.372448	-0.600088
23	9	0	0.694055	6.496539	2.430388
24	6	0	4.759326	-1.273077	-0.814584
25	6	0	-3.069862	-3.742224	-0.862507
26	1	0	-4.085691	-4.110944	-1.005201
27	6	0	-4.973785	-1.319717	-0.538250
28	6	0	-0.095245	6.720208	0.195412
29	6	0	-5.670238	-1.957110	0.508464
30	6	0	-1.370435	1.744604	-0.213327
31	6	0	5.423220	-0.761244	-1.949163
32	6	0	-2.915007	0.100842	-0.371628

33	6	0	-3.489820	-1.189427	-0.500436
34	6	0	-0.111132	3.887477	-0.047459
35	6	0	-5.744103	-0.834397	-1.614550
36	6	0	6.811273	-0.881652	-2.117433
37	6	0	6.944992	-2.066827	-0.002063
38	6	0	-0.809086	-3.586815	-0.716541
39	6	0	5.557570	-1.926209	0.146378
40	6	0	-0.112323	2.397838	-0.170082
41	6	0	-1.891788	-4.491065	-0.936193
42	1	0	-1.807469	-5.558260	-1.141222
43	6	0	-2.674163	2.360676	-0.169514
44	1	0	-2.860446	3.430087	-0.077960
45	6	0	0.616373	-3.582004	-0.732589
46	6	0	-7.140548	-0.971069	-1.649761
47	6	0	-7.063793	-2.112689	0.493684
48	6	0	-3.616054	1.356084	-0.266111
49	1	0	-4.699628	1.469524	-0.267927
50	6	0	7.573986	-1.539842	-1.140463
51	6	0	-7.800968	-1.615641	-0.592372
52	6	0	0.307559	5.920061	1.275695
53	6	0	3.282817	-1.160314	-0.646026
54	6	0	-0.504872	4.720416	-1.114057
55	6	0	-0.505811	6.119805	-1.004718
56	6	0	1.695995	-4.474885	-1.005383
57	1	0	1.611248	-5.540312	-1.219242
58	6	0	3.390038	1.392366	-0.478398
59	1	0	4.467705	1.520965	-0.572655
60	6	0	2.702785	0.125827	-0.492419
61	6	0	0.291972	4.523547	1.143153
62	6	0	2.508613	-2.351582	-0.689053
63	6	0	2.869363	-3.716025	-0.978503
64	1	0	3.880419	-4.074294	-1.172142
65	6	0	1.149128	1.755455	-0.266745
66	6	0	0.617664	-1.011926	3.139397
67	6	0	-1.527259	-1.245090	2.732520
68	6	0	-1.389715	-1.312532	4.100370
69	7	0	-0.030768	-1.161755	4.338361
70	1	0	0.420644	-1.172770	5.249560
71	1	0	-2.431521	-1.334127	2.134232
72	1	0	-2.108124	-1.457741	4.902792
73	7	0	-0.281547	-1.057766	2.145275
74	6	0	2.103133	-0.798467	3.017410
75	6	0	2.490640	0.663151	3.348934
76	6	0	2.901590	-1.801527	3.878656

77	1	0	2.279003	0.901150	4.407182
78	1	0	3.569876	0.814957	3.180344
79	1	0	1.941016	1.379954	2.719343
80	1	0	2.756549	-1.621802	4.960606
81	1	0	2.614868	-2.843058	3.660102
82	1	0	3.978528	-1.695889	3.673815
83	1	0	2.346931	-0.986807	1.958466

(TPFC)Mn^{III}(4-IPi)

1	25	0	0.087679	-0.876937	-0.165594
2	7	0	-1.152867	-2.283424	-0.588005
3	7	0	1.530777	0.402308	-0.333092
4	7	0	1.329677	-2.285316	-0.586992
5	9	0	-4.970233	-2.432862	1.254781
6	7	0	-1.346054	0.406728	-0.340377
7	9	0	-4.768293	-0.080816	-2.899062
8	9	0	-7.661244	-2.690962	0.967227
9	9	0	-7.462614	-0.322446	-3.156551
10	9	0	-8.921985	-1.632892	-1.233569
11	9	0	5.165513	-0.176251	-2.667257
12	9	0	9.128118	-1.723993	-0.581256
13	9	0	0.863717	4.234147	-2.235550
14	9	0	7.871035	-0.456424	-2.667945
15	9	0	0.861359	6.940434	-1.954909
16	9	0	7.656279	-2.696540	1.526944
17	9	0	0.078358	8.078874	0.419368
18	9	0	-0.673093	3.779635	2.262577
19	9	0	4.952605	-2.395583	1.557938
20	6	0	2.658828	2.390258	-0.137476
21	1	0	2.843308	3.458174	-0.026828
22	6	0	-2.518521	-2.317498	-0.743588
23	9	0	-0.692985	6.487377	2.521212
24	6	0	4.963974	-1.281713	-0.559479
25	6	0	-2.879556	-3.674791	-1.064377
26	1	0	-3.892127	-4.030317	-1.254938
27	6	0	-4.772784	-1.243064	-0.810029
28	6	0	0.083581	6.741033	0.285338
29	6	0	-5.554590	-1.912131	0.153587
30	6	0	-1.162931	1.781299	-0.243503
31	6	0	5.750439	-0.791499	-1.621571
32	6	0	-2.715063	0.152642	-0.482112
33	6	0	-3.294155	-1.130023	-0.660115
34	6	0	0.095842	3.912551	0.003170
35	6	0	-5.453292	-0.714930	-1.926750

36	6	0	7.147256	-0.930783	-1.637202
37	6	0	7.038029	-2.083635	0.498922
38	6	0	-0.624249	-3.541689	-0.840965
39	6	0	5.645238	-1.924808	0.492989
40	6	0	0.097504	2.424590	-0.140582
41	6	0	-1.705041	-4.429852	-1.124505
42	1	0	-1.620648	-5.489283	-1.366354
43	6	0	-2.458044	2.412851	-0.300877
44	1	0	-2.633550	3.487219	-0.259006
45	6	0	0.801317	-3.544314	-0.833377
46	6	0	-6.843406	-0.835002	-2.076528
47	6	0	-6.944087	-2.052119	0.022996
48	6	0	-3.404605	1.417235	-0.440125
49	1	0	-4.483505	1.544550	-0.520308
50	6	0	7.791512	-1.582499	-0.574138
51	6	0	-7.590316	-1.508844	-1.098018
52	6	0	-0.313663	5.926368	1.356780
53	6	0	3.479441	-1.151440	-0.539958
54	6	0	0.484381	4.759637	-1.054057
55	6	0	0.486726	6.157333	-0.925510
56	6	0	1.885353	-4.442588	-1.068822
57	1	0	1.802537	-5.504759	-1.299111
58	6	0	3.602387	1.388783	-0.250102
59	1	0	4.685844	1.504012	-0.249941
60	6	0	2.902947	0.135060	-0.382608
61	6	0	-0.300237	4.531572	1.205256
62	6	0	2.699787	-2.332144	-0.680433
63	6	0	3.063332	-3.695374	-0.971706
64	1	0	4.079892	-4.060495	-1.118957
65	6	0	1.355892	1.773756	-0.194860
66	6	0	1.524540	-1.426143	2.582208
67	6	0	-0.579298	-1.261885	3.186478
68	6	0	0.141831	-1.612666	4.315479
69	7	0	1.466350	-1.708331	3.912809
70	1	0	2.256611	-1.964867	4.499262
71	7	0	0.305453	-1.150182	2.111929
72	1	0	-0.161299	-1.800933	5.341736
73	1	0	2.445064	-1.454161	2.001883
74	6	0	-2.056244	-0.981480	3.056654
75	6	0	-2.354517	0.523003	3.260311
76	6	0	-2.892117	-1.845174	4.021749
77	1	0	-2.343404	-1.249246	2.023786
78	1	0	-1.766878	1.151778	2.573251
79	1	0	-3.423617	0.730632	3.083332

80	1	0	-2.113133	0.828818	4.294105
81	1	0	-2.684264	-2.919634	3.886918
82	1	0	-2.688311	-1.584801	5.076430
83	1	0	-3.967231	-1.680328	3.843910

(TPFC)Mn^{III}(5-IPi)

1	25	0	0.006560	-1.023249	-0.219466
2	7	0	-1.240672	-2.475713	-0.385602
3	7	0	1.451445	0.218094	-0.535942
4	7	0	1.239197	-2.485311	-0.411185
5	9	0	-4.954575	-2.454563	1.558682
6	7	0	-1.424813	0.229745	-0.565727
7	9	0	-4.975844	-0.480707	-2.793952
8	9	0	-7.653604	-2.729662	1.436702
9	9	0	-7.678255	-0.731400	-2.883448
10	9	0	-9.032369	-1.863311	-0.777769
11	9	0	4.953408	-0.596051	-2.870780
12	9	0	9.031244	-1.959129	-0.883381
13	9	0	-0.795544	3.900280	-2.797089
14	9	0	7.652384	-0.878081	-2.999627
15	9	0	-0.779836	6.618200	-2.725506
16	9	0	7.683121	-2.744207	1.379183
17	9	0	0.072941	7.934770	-0.470037
18	9	0	0.867113	3.789173	1.682157
19	9	0	4.987689	-2.438701	1.537369
20	6	0	2.584421	2.206125	-0.675722
21	1	0	2.772988	3.276529	-0.751441
22	6	0	-2.609632	-2.522966	-0.504195
23	9	0	0.899686	6.505102	1.727350
24	6	0	4.872650	-1.501728	-0.659393
25	6	0	-2.979857	-3.909234	-0.622134
26	1	0	-3.996867	-4.283842	-0.738636
27	6	0	-4.864796	-1.453768	-0.612304
28	6	0	0.060281	6.590687	-0.499813
29	6	0	-5.594316	-2.033746	0.446434
30	6	0	-1.243172	1.606311	-0.581602
31	6	0	5.597385	-1.113113	-1.805246
32	6	0	-2.797942	-0.037407	-0.566936
33	6	0	-3.381816	-1.329707	-0.551346
34	6	0	0.032887	3.746152	-0.562428
35	6	0	-5.605848	-1.022737	-1.732943
36	6	0	6.990757	-1.256430	-1.889370
37	6	0	7.005439	-2.218090	0.340435
38	6	0	-0.718948	-3.760851	-0.464126

39	6	0	5.613315	-2.056997	0.404519
40	6	0	0.021071	2.252619	-0.582508
41	6	0	-1.807784	-4.673182	-0.596630
42	1	0	-1.732628	-5.756978	-0.686221
43	6	0	-2.543738	2.231167	-0.587085
44	1	0	-2.725693	3.305251	-0.594045
45	6	0	0.708367	-3.765505	-0.471695
46	6	0	-7.001888	-1.149844	-1.796900
47	6	0	-6.988571	-2.179545	0.401942
48	6	0	-3.490881	1.226938	-0.580038
49	1	0	-4.573642	1.347347	-0.579214
50	6	0	7.696367	-1.813708	-0.811992
51	6	0	-7.695084	-1.733162	-0.725277
52	6	0	0.485794	5.859096	0.619856
53	6	0	3.391255	-1.361401	-0.577130
54	6	0	-0.382866	4.512285	-1.670217
55	6	0	-0.378581	5.915906	-1.649355
56	6	0	1.789372	-4.689485	-0.594715
57	1	0	1.704640	-5.773576	-0.670770
58	6	0	3.523314	1.193178	-0.667570
59	1	0	4.605927	1.303088	-0.717979
60	6	0	2.821371	-0.062875	-0.588036
61	6	0	0.462631	4.457843	0.575189
62	6	0	2.607837	-2.545577	-0.521118
63	6	0	2.967188	-3.936610	-0.625560
64	1	0	3.981662	-4.320668	-0.732556
65	6	0	1.280396	1.594961	-0.594231
66	6	0	-0.427678	-1.738382	2.891010
67	6	0	0.261095	0.324868	2.760995
68	6	0	0.045899	0.087555	4.107531
69	7	0	-0.392439	-1.235984	4.160276
70	1	0	-0.638102	-1.746039	5.005844
71	1	0	0.599126	1.237671	2.275446
72	7	0	-0.035256	-0.810916	2.020554
73	1	0	-0.735103	-2.752288	2.643620
74	6	0	0.167630	0.955026	5.335496
75	6	0	-1.223664	1.304620	5.919529
76	6	0	0.977340	2.229526	5.031170
77	1	0	0.721473	0.376784	6.104303
78	1	0	-1.811329	0.401587	6.158697
79	1	0	-1.116233	1.892412	6.846947
80	1	0	-1.805822	1.901727	5.197331
81	1	0	1.987809	1.986180	4.664408
82	1	0	0.476634	2.845500	4.265126

83	1	0	1.078891	2.842829	5.941550
(TPFC)Mn ^{III}					
1	25	0	-0.002426	-1.010443	-0.009901
2	7	0	-1.242154	-2.449513	-0.064778
3	7	0	1.433951	0.242849	0.016752
4	7	0	1.232539	-2.454606	-0.039132
5	9	0	-4.940560	-2.508696	2.014730
6	7	0	-1.434793	0.247380	0.018143
7	9	0	-5.008120	-0.386630	-2.264036
8	9	0	-7.644909	-2.769166	1.918750
9	9	0	-7.714321	-0.629324	-2.331909
10	9	0	-9.045707	-1.826323	-0.248499
11	9	0	5.056057	-0.366633	-2.153118
12	9	0	9.041194	-1.854195	-0.069667
13	9	0	0.803776	3.968355	-2.052443
14	9	0	7.762064	-0.616629	-2.162051
15	9	0	0.819889	6.685835	-1.912875
16	9	0	7.587681	-2.829764	2.047813
17	9	0	0.016745	7.951739	0.389122
18	9	0	-0.791758	3.758316	2.441310
19	9	0	4.883152	-2.561652	2.086195
20	6	0	2.562487	2.231418	0.180723
21	1	0	2.748969	3.300795	0.270847
22	6	0	-2.616741	-2.502511	-0.105370
23	9	0	-0.792863	6.477248	2.560561
24	6	0	4.873462	-1.453076	-0.031435
25	6	0	-2.983729	-3.890353	-0.194225
26	1	0	-4.003444	-4.270892	-0.248204
27	6	0	-4.879068	-1.435609	-0.119799
28	6	0	0.013438	6.609479	0.325127
29	6	0	-5.595196	-2.047073	0.929915
30	6	0	-1.256730	1.628893	0.074518
31	6	0	5.651507	-0.965195	-1.101989
32	6	0	-2.814543	-0.022604	-0.012268
33	6	0	-3.394163	-1.313127	-0.075664
34	6	0	0.005854	3.771178	0.189997
35	6	0	-5.630125	-0.965246	-1.216829
36	6	0	7.048819	-1.089792	-1.123426
37	6	0	6.959149	-2.228078	1.020929
38	6	0	-0.719014	-3.740588	-0.127260
39	6	0	5.563595	-2.084732	1.024011
40	6	0	0.002581	2.278040	0.118677
41	6	0	-1.809111	-4.652419	-0.205474

42	1	0	-1.736937	-5.738050	-0.267032
43	6	0	-2.558381	2.244525	0.080307
44	1	0	-2.742493	3.317649	0.111565
45	6	0	0.705400	-3.743304	-0.116435
46	6	0	-7.026953	-1.086258	-1.268798
47	6	0	-6.990807	-2.186706	0.896816
48	6	0	-3.504350	1.238655	0.033423
49	1	0	-4.587014	1.357655	0.035180
50	6	0	7.703786	-1.726180	-0.057656
51	6	0	-7.708530	-1.701814	-0.207489
52	6	0	-0.403187	5.854498	1.432602
53	6	0	3.388761	-1.326151	-0.020246
54	6	0	0.414297	4.558840	-0.904965
55	6	0	0.426412	5.960967	-0.849146
56	6	0	1.792918	-4.658756	-0.187653
57	1	0	1.717433	-5.743710	-0.256743
58	6	0	3.505425	1.222313	0.140948
59	1	0	4.587532	1.334780	0.193962
60	6	0	2.812511	-0.033646	0.036414
61	6	0	-0.398533	4.453407	1.354843
62	6	0	2.607297	-2.512449	-0.067419
63	6	0	2.970102	-3.901120	-0.160010
64	1	0	3.988887	-4.285050	-0.207009
65	6	0	1.259704	1.623366	0.101495