Journal of Physical & Theoretical Chemistry
Islamic Azad University of Iran 3 (1)
(2006)
Science and Research Campus
ISSN: 1735-2126

Theoretical Study of CrO_4^{2-} and MoO_4^{2-} Interaction with Glysine via Comparing NMR, NBO and other chemical factors

Majid Monajjemi[1] , Roya Ahmadi [1,2] , K.Zare[1,4] , Elahe Rejaian[3]

[1] Science and Research campus, Islamic Azad University, P. O .Box 14515- 775, Tehran, Iran
[2] Shahr-e-rey Branch , Islamic Azad University, Shahr-e-rey, Iran
[3] Arak Branch, Islamic Azad University
[4] Shahid Beheshti University

ABSTRACT

In this paper geometry optimization of two ionic complexes such as CrO_4^{2-} Gly^{+1}, and MoO_4^{2-} Gly^{+1} have been carried out at the *HF* and *B3LYP* levels of theory with $6-31G*$ basis set in the gas phase. Moreover, chemical shift and natural bond of orbital *(NBO)* of these compounds have been obtained using *NMR* and *NBO* methods. Finally, the obtained theoretical results were compared with each other.

INTRODUCTION

Trace amounts of Cr and Mo are essential nutrient (1). Chromium (III) is an essential trace mineral Chromium III complexes with other components (not completely characterized) to form glucose tolerance factor (GTF). GTF facilitates the binding of insulin to its cell membrane receptor that involved in helping insulin to metabolize fat, utilize protein and convert sugar into energy (36). Molybdenum (Mo) is necessary for the enzymes that reduce nitrate in plants and for the enzyme nitrogenase which is the key enzyme in biological nitrogen fixation (2). Many chromium-containing (Cr) compounds are use for plating, manufacturing, paints and dyes, tanning leather and preserving wood. On the other hand, Cr (VI) is known to have an adverse affect on the lungs, liver and kidneys (3). Autopsy of a 14-year old boy who had ingested 7.5 mg Cr (VI) revealed enlarged brain and cerebral edema. However, this effect may be secondary to kidney failure rather than a direct effect on the nervous system (37). CrO_3 and MoO_3 are strongly acidic and dissolve in aqueous $NaOH$ forming discrete tetrahedral CrO_4^{2-} and MoO_4^{2-} ions. CrO_4^{2-}, and MoO_4^{2-} exist both in solution and as solid. CrO_4^{2-} is strong oxidizing agent, but MoO_4^{2-} has weak oxidizing powers. Acidification of aqueous of the yellow, tetrahedral chromate ion, CrO_4^{2-} initiates a series of labile equilibria involving the formation of the orange-red-dichromate ion $Cr_2O_7^{2-}$. Above pH 8 only CrO_4^{2-} ions exist in appreciable concentration but, as the pH is lowered, the equilibria shift and between pH 2-6, the $HCrO_4^{1-}$ and $Cr_2O_7^{2-}$ ions are in equilibrium. In aqueous solution, equilibration of the molybdenum species is complete within a matter of minutes, undoubtedly the first major polyanion formed when the pH of an aqueous molybdate solution is reduced below about 6 is the heptamolybdate $[Mo_7O_{24}]^{-6}$, traditionally known as the paramolybdate. Anions with 8 and 36 Mo atoms (14) are formed before the increasing acidity suffices to precipitate the hydrous oxide. The formation of these isopolyanions may be represented by the net equations.

this paper by using ab initio calculations and a quantum chemical approach, we worked on optimizing of coordination systems of CrO_4^{2-} and MoO_4^{2-} with glysine In ion states, also computed various tensors of *NMR* and natural bond order(*NBO*) of them, finally compared the results of them.

COMPUTATIONAL DETAILS

In this report, all calculations of coordination compounds have been done in gas phase. The calculations for C,H,N,O atoms have been performed by the standard $6-31G^*$ Basis set for Cr,Mo standard *LANL2DZ* basis sets have been considered. All system have been optimized at Hartree Fock (*HF*) and Beck3lyp Density Functional Theory (DFT) (19-23).The natural bond orbital (NBO) analyses have been performed using the NBO as implemented in the GAUSSIAN 03(24-32). The chemical shift calculations ($\sigma_{11}, \sigma_{22}, \sigma_{33}, \sigma_{iso}, \sigma_{aniso}$) have been performed by *NMR* keyword and finally we compared obtained results according to tables and plots. For comparing the results some parameters have been calculated such as chemical shift δ, the shielding tensor asymmetry parameter ($\Delta\eta$), the anisotropy ($\Delta\sigma$) of the tensor, and the effective $\Delta\sigma$ which are defined as (17, 18, and 19) .

$$\delta = \frac{\sigma_{11} + \sigma_{22}}{[\sigma_{33} - \sigma_{iso}]} \quad (1)$$

$$\Delta\eta = \frac{\sigma_{22} - \sigma_{11}}{\sigma_{33} + \sigma_{iso}} \quad (2)$$

$$\Delta\sigma = \sigma_{33} - \frac{1}{2}(\sigma_{11} + \sigma_{22}) \quad (3)$$

$$\Delta\sigma_{eff} = (\sigma_{11}^2 + \sigma_{22}^2 + \sigma_{33}^2 - \sigma_{11}\sigma_{22} - \sigma_{11}\sigma_{33} - \sigma_{22}\sigma_{33})^{\frac{1}{2}} \quad (4)$$

Also in this paper Chemical shift anisotropy (*CSA*) and (CSA_a) were considered as:

$$CSA = \Delta\sigma \quad (5)$$

$$CSA_a = \Delta\sigma_{eff} \quad (6)$$

RESULTS AND DISCUSSION

In this research to study complex formation, the GLY^{+1} has been placed around the, $CrO4^{2-}$ and $MoO4^{2-}$ .this work was done with dummy atom method. Since these anions are tetrahedral, so we can consider similar interaction for them for optimization. All optimizations have been performed at the Hartree Fock level

(HF) and becke-3lyp density function theory (DFT). These anions were closed to GLY^{+1} from near of NH_3 in $GLY^{+1}=NH_3CH_2COOH$) due to the positive charge on the nitrogen of NH_3 in GLY^{+1}.We optimized these systems step by step. As a first step those were optimized in the low basis set and then were optimized by the high basis set ($sto-3g,3-21g,3-21g*,6-31g*$). In all of case for Cr and Mo standard lanl2dz basis sets were used.

The N of NH_3^+ near the GLY, this position was considered, because the positive charge is there. This position was considered the best case for the adjacent anions($CrO4^{2-}$ and $MoO4^{2-}$).

In the processing of optimization of these compounds one of the hydrogen of NH_3^+ was disconnected from N and was connected to one the oxygen of these anions. That was considered that the reason of this phenomenon is formation of hydrogen bond between them. So the bond lengths of $N-H$ of NH_3^+ were considered fix in the processing of optimizing through freezing method. After optimization the chemical shift of their atoms were computed by NMR method and natural orbital bond of them were computed by (NBO) method.

These results are reported in the table$(1-3)$, and then were computed $CSA, CSA_a, \delta, \Delta\eta$ by the relevant formulas of them. These results are reported in the tables$(4-7)$.

According to some of these factors which have been compared, the results show that in $CrO_4^{2-}Gly^{1+}$ and $MoO_4^{2-}Gly^{1+}$ with decreasing the negative atomic charge of O_{13}, O_{14} the CSA, CSA_a of them increase but the delta(δ) of them increase with increasing the negative atomic charge of them.

Also the results show for $H_8, H_9, H_{10}, H_{11}, H_{15}$ and H_{16} that with increasing the positive atomic charge of them CSA, CSA_a increase but the delta (δ) of them decrease, except for one or two points.

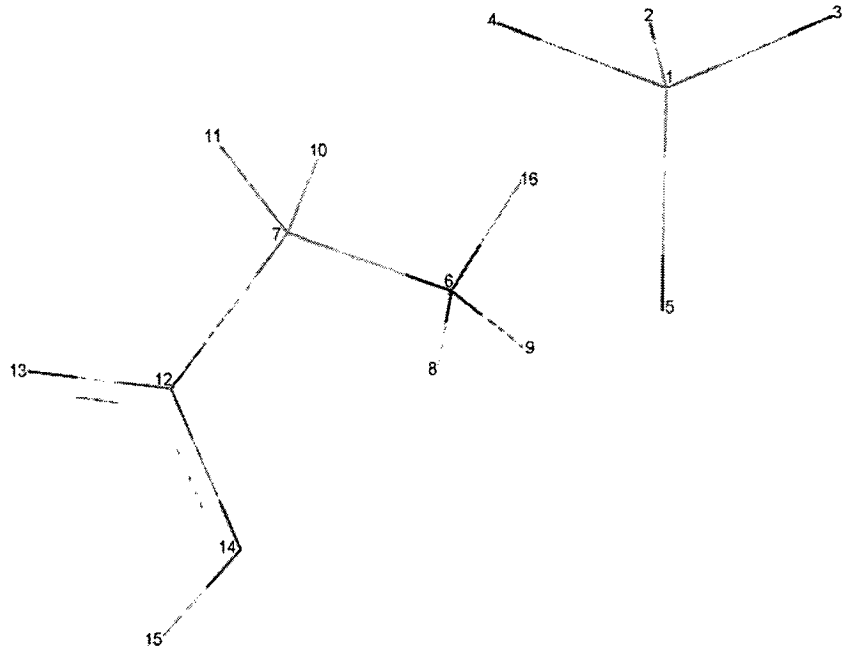
Fig (3, 8) show with increasing the contribution of $(p\&d)$ orbital in σ bonds of C_7-H_{10}, C_7-H_{10}, M_1-O_3 and, M_1-O_4 the bond lengths of them decrease but for $C_{12}-O_{13}$ and $C_{12}-O_{14}$ the bond lengths increase.

The results turn out that the interaction energy of $MoO_4^{2-}Gly^{1+}$ is lower than $CrO_4^{2-}Gly^{1+}$ in the same condition. For example that is $-4520/3282684$ for $HF/6-31G*$ of $MoO_4^{2-}Gly^{1+}$ where as it is $-1616/3469182$ for $HF/6-31G*$ of $CrO_4^{2-}Gly^{1+}$.

CONCLUSION

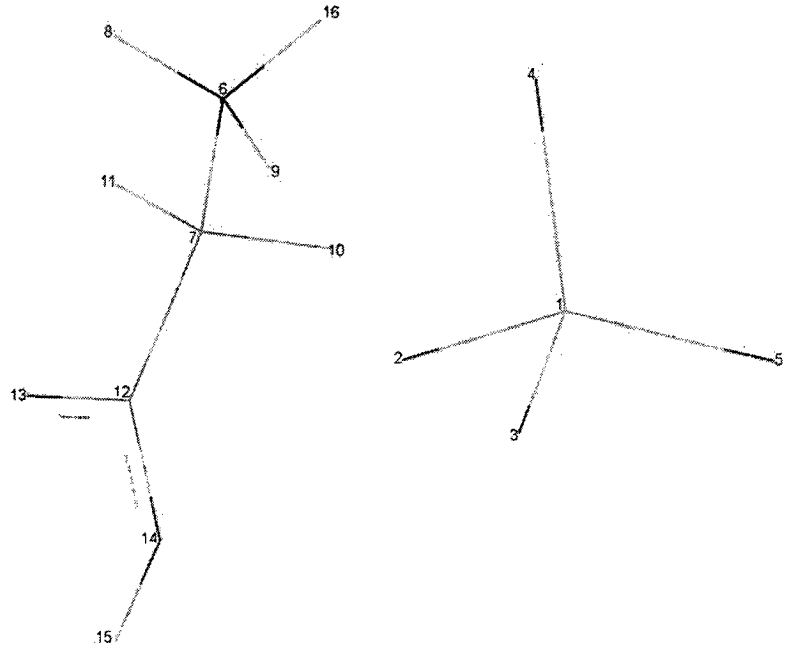
The same complexes containing Cr and Mo atoms reveal an interesting reflection of increasing tendency toward formation of MO_4 in the order $Mo^{VI} > Cr^{VI}$. Their structures hold tetrahedral geometry.

For $MoO_4^{2-}Gly^{1+}$ the bond length of $Mo-O$ bond is smaller than $Cr-O$ bond of $CrO_4^{2-}Gly^{1+}$. So the bond lengths of $M-O$ of these structures decrease in the order $Cr > Mo$. The maximum multiple bonds of $M-O$ exist in the order $MoO_4^{2-} > CrO_4^{2-}$ also the stabilities of these structures have the same ordering. So, considering the stabilities of these compounds depends on the further providing of the ability of oxygen- metal to form multiple bonds.



No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Atom	Cr	O	O	O	O	N	C	H	H	H	H	C	O	O	H	H

Figure1. The structure of $CrO4^{2-}GLY^{1+}$ after optimization.



No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Atom	Mo	O	O	O	O	N	C	H	H	H	H	C	O	O	H	H

Figure2. The structure of $MoO4^{2-}GLY^{1+}$ after optimization.

Table1: Selected optimized parameters of CrO_4^{2-} Gly^{+1} and MoO_4^{2-} Gly^{+1} ionic complexes (angstroms and degrees).

	compound	r(1, 2)	r(1, 3)	r(1, 4)	r(6, 7)	r(7, 10)	r(7, 11)	r(7, 12)	r(12, 13)	r(12, 14)	r(14, 15)
HF	*GLY*	-	-	-	1.4961	1.0804	1.0805	1.5170	1.1847	1.3010	0.9569
	CrO_4^{2-}	1.5968	1.5968	1.5968	-	-	-	-	-	-	-
	$CrO_4^{2-}GLY$	1.6400	1.5478	1.5838	1.4691	1.0884	1.0815	1.5043	1.1864	1.3307	0.9519
	MoO_4^{2-}	1.7628	1.7628	1.7628	-	-	-	-	-	-	-
	$MoO_4^{2-}GLY$	1.7904	1.7313	1.7894	1.4775	1.0629	1.0828	1.4999	1.1952	1.3084	0.9507
B3LYP	*GLY*	-	-	-	1.5090	1.0926	1.0926	1.5282	1.2101	1.3228	0.9794
	CrO_4^{2-}	1.6480	1.6480	1.6480	-	-	-	-	-	-	-
	$CrO_4^{2-}GLY$	1.6833	1.6044	1.6553	1.4865	1.1287	1.0926	1.4969	1.2110	1.3635	0.9754
	MoO_4^{2-}	1.8072	1.8072	1.8072	-	-	-	-	-	-	-
	$MoO_4^{2-}GLY$	1.8497	1.7652	1.8242	1.4991	1.0863	1.0918	1.5146	1.2340	1.3519	0.9750
	compound	A(2,1,3)	A(2,1,4)	A(2,1,5)	A(7, 6,8)	A(7,12,14)	A(12,14,15)	A(13,12,14)	D(11,7,12,14)	D(7,12,14,15)	D(13,12,14,15)
HF	*GLY*	-	-	-	110.9	111.4	111.3	127.8	-61.2	-180.0	0.0
	CrO_4^{2-}	109.5	109.5	109.5	-	-	-	-	-	-	-
	$CrO_4^{2-}GLY$	112.2	107.6	104.5	113.8	113.7	107.9	122.5	126.3	-176.1	-5.1
	MoO_4^{2-}	109.5	109.5	109.5	-	-	-	-	-	-	-
	$MoO_4^{2-}GLY$	108.0	104.6	112.8	103.6	112.3	108.2	124.2	78.8	177.6	-17.0
B3LYP	*GLY*	-	-	-	110.4	111.0	109.6	128.1	-61.5	180.0	-0.0
	CrO_4^{2-}	109.5	109.5	109.5	-	-	-	-	-	-	-
	$CrO_4^{2-}GLY$	112.6	107.1	104.3	113.5	113.0	105.7	122.1	134.7	175.5	-4.2
	MoO_4^{2-}	109.5	109.5	109.5	-	-	-	-	-	-	-
	$MoO_4^{2-}GLY$	112.3	108.0	112.4	101.9	112.4	103.3	121.9	83.7	-167.3	-17.5

Table2: The chemical shielding data of $CrO_4^{-2}GLY^{+1}$ and, $MoO_4^{-2}GLY^{+1}$ complexes, calculated by NMR method at the levels of HF/6-31G(d) and B3LYP/6-31G(d).

	$CrO_4^{2-}GLY(HF)$					$CrO_4^{2-}GLY(B3LYP)$				
atom	σ_{11}	σ_{22}	σ_{33}	σ_{iso}	σ_{aniso}	σ_{11}	σ_{22}	σ_{33}	σ_{iso}	σ_{aniso}
1*Cr*	-6756.8945	-6340.6388	-5931.6481	-6343.0604	617.1185	-393.5018	-333.1012	-279.6736	-335.4255	83.6279
2*O*	-1408.1580	-640.5870	177.4253	-623.7732	1201.7979	-269.8512	-3.2210	256.4074	-5.5549	-392.9435
3*O*	-2475.2247	-1773.6225	84.8238	-1388.0078	2209.2474	-434.5604	-416.6409	145.3464	-235.2850	570.9470
4*O*	-2284.3048	-1086.3657	159.5689	-1069.7005	1843.9041	-300.7515	-151.0836	-3.2380	-151.6910	222.6796
5*O*	-1514.4273	-670.7814	180.2807	-668.3094	1272.8850	-300.1625	-16.1078	245.3304	-23.6466	403.4655
6*N*	224.3768	241.6558	274.3996	246.8108	41.3833	285.3775	297.3098	333.6973	305.4615	42.3536
7*C*	142.8267	164.3644	182.1148	163.1019	28.5192	175.1250	182.0523	205.5452	187.5742	26.9566
8*H*	26.2438	28.2009	39.4227	31.2891	12.2003	25.1129	28.2208	42.1933	31.8423	15.5264
9*H*	2.5089	19.3882	39.1347	20.3439	28.1862	10.1466	17.9253	41.2731	23.1150	27.2372
10*H*	11.8612	24.8193	33.8988	23.5264	15.5585	18.6036	21.2286	35.3649	25.0657	15.4488
11*H*	22.6828	31.0106	34.9186	29.5373	8.0719	24.3565	29.4235	36.3911	30.0570	9.5011
12*C*	-63.0745	71.3367	106.7594	38.3405	102.6283	42.6815	149.7137	174.4345	122.2766	78.2369
13*O*	-262.5070	-148.7091	326.3539	-28.2874	531.9620	-367.0137	-97.3251	400.9819	-21.1190	633.1513
14*O*	47.0962	208.3118	303.0800	186.1627	175.3760	93.0891	260.5877	286.7136	213.4635	109.8752
15*H*	23.3158	23.8177	36.0228	27.7188	12.4560	23.1928	27.2773	35.3543	28.6081	10.1192
16*H*	0.1547	18.5967	41.4436	20.0648	32.0681	8.7302	17.2665	43.1542	23.0503	30.1558
	$MoO_4^{2-}GLY(HF)$					$MoO_4^{2-}GLY(B3LYP)$				
atom	σ_{11}	σ_{22}	σ_{33}	σ_{iso}	σ_{aniso}	σ_{11}	σ_{22}	σ_{33}	σ_{iso}	σ_{aniso}
1*Mo*	954.0567	1006.5066	1143.1683	1034.5772	162.8867	807.9530	858.6407	926.3936	864.3291	93.0962
2*O*	-406.7314	-216.5602	77.5552	-181.9121	389.2011	-355.6913	-295.0867	-126.5538	-259.1106	198.8352
3*O*	-880.9502	-462.8386	-31.7678	-458.5189	640.1266	-831.3761	-485.7514	-277.9829	-531.7035	380.5809
4*O*	-492.8430	-206.0640	79.5259	-206.4604	428.9794	-515.0802	-286.8308	-92.8263	-298.2458	308.1292
5*O*	-933.8230	-648.0771	-42.2105	-541.3702	748.7395	-879.1123	-623.1534	-243.4812	-581.9156	507.6517
6*N*	220.4927	231.1551	273.5559	241.7346	47.7320	179.4996	205.6803	264.6535	216.6112	72.0635
7*C*	144.3541	152.6222	176.7050	157.8938	28.2169	121.3826	137.0578	156.1482	138.1962	26.9280
8*H*	15.0740	16.4856	37.4390	22.9995	21.6592	15.2587	17.3130	36.5422	23.0380	20.2564
9*H*	12.7820	17.9938	39.2196	23.3318	23.8317	11.7575	18.2721	37.8634	22.6310	22.8486
10*H*	17.5694	25.2595	32.0839	24.9709	10.6694	13.9650	24.0850	31.0660	23.0387	12.0410
11*H*	26.1247	29.8378	34.6310	30.1978	6.6497	26.1799	29.1335	32.9176	29.4103	5.2609
12*C*	-54.4228	63.2619	107.9777	38.9389	103.5581	-33.3490	74.4253	83.4372	41.5045	62.8991
13*O*	212.0334	-80.5147	328.1927	11.8815	474.4667	-130.0396	-50.6188	260.5014	26.6143	350.8306
14*O*	59.8253	218.3511	298.8734	192.3499	159.7852	39.9419	137.6839	272.1170	149.9143	183.3041
15*H*	23.1132	23.4605	36.7943	27.7893	13.5075	24.9456	26.0062	34.1788	28.3769	8.7029
16*H*	24.6636	27.2782	40.2802	30.4707	14.3093	24.9983	27.6588	37.9438	30.2003	11.6152

Table3: The chemical shielding data of CrO_4^{-2} and MoO_4^{-2} complexes, calculated by NMR method at the levels of HF/6-31G (d) and B3LYP/6-31G (d).

	$CrO_4^{2-}GLY(HF)$					$CrO_4^{2-}GLY(B3LYP)$				
	σ_{11}	σ_{22}	σ_{33}	σ_{iso}	σ_{aniso}	σ_{11}	σ_{22}	σ_{33}	σ_{iso}	σ_{aniso}
1*Cr*	-4686.6412	-4686.4612	-4686.6412	-4686.6412	0.00000	-2329.4761	-2329.4761	-2329.4276	-2329.4599	0.0485
2*O*	-1264.6003	-1264.6003	223.3753	-768.6085	1487.9756	-554.2738	-554.2698	-109.1927	-405.9121	445.0791
3*O*	-1264.6003	-1264.6003	223.3753	-768.6085	1487.9756	-554.2738	-554.2698	-109.1927	-405.9121	445.0791
4*O*	-1264.6003	-1264.6003	223.3753	-768.6085	0.00000	-554.2738	-554.2698	-109.1927	-405.9121	445.0791
5*O*	-1264.6003	-1264.6003	223.3753	-768.6085	1487.9756	-554.2738	-554.2698	-109.1927	-405.9121	445.0791
	$MoO_4^{2-}GLY(HF)$					$MoO_4^{2-}GLY(B3LYP)$				
	σ_{11}	σ_{22}	σ_{33}	σ_{iso}	σ_{aniso}	σ_{11}	σ_{22}	σ_{33}	σ_{iso}	σ_{aniso}
Mo	1110.3682	1110.3682	1110.3682	1110.3682	0.000000	897.0033	897.0033	897.0033	897.0033	0.00000
2*O*	-473.6142	-473.6142	52.7218	-298.1688	526.3359	-443.3340	-443.3340	-118.1234	-334.9305	325.2106
3*O*	-473.6142	-473.6142	52.7218	-298.1688	526.3359	-443.3340	-443.3340	-118.1234	-334.9305	325.2106
4*O*	-473.6142	-473.6142	52.7218	-298.1688	526.3359	-443.3340	-443.3340	-118.1234	-334.9305	325.2106
5*O*	-473.6142	-473.6142	52.7218	-298.1688	526.3359	-443.3340	-443.3340	-118.1234	-334.9305	325.2106

Table4: Summary of representative computed shielding tensor elements of $CrO_4^{-2}GLY^{+1}$ and $MoO_4^{-2}GLY^{+1}$ complexes, calculated by NMR method at the levels of HF/6-31G(d) and B3LYP/6-31G(d).

	$CrO_4^{2-}GLY(HF)$				$CrO_4^{2-}GLY(B3LYP)$			
	CSA	CSA_a	δ	$\Delta\eta$	*CSA*	CSA_a	δ	$\Delta\eta$
1*Cr*	617.1186	714.6936	-31.8356	-0.0339	83.6279	98.6397	-13.0328	-0.09820
2*O*	1201.7978	1373.3870	-2.5571	-1.7197	392.9435	455.7668	-1.0424	1.0629
3*O*	2209.2474	2291.2787	-2.8848	-0.5384	570.9471	571.1580	-2.2363	-0.1992
4*O*	1844.9042	2116.5928	-2.7420	-1.3162	222.6796	257.6559	-3.0436	-0.9660
5*O*	1272.8851	1467.6649	-2.5751	-1.7287	403.4656	472.5460	-1.1758	-1.2814
6*N*	41.3833	44.0057	16.8921	0.03315	42.3537	43.5961	20.6364	0.01867
7*C*	28.5193	34.0771	16.1570	0.06239	26.9566	27.6161	19.8752	0.01762
8*H*	12.2004	12.3175	6.6938	0.0277	15.5264	15.7580	5.1525	0.0420
9*H*	28.1862	31.7513	1.1653	0.2838	27.2372	28.0579	1.5460	0.1208
10*H*	15.5586	19.1834	3.5364	0.2256	15.4488	15.6152	3.8675	0.0434
11*H*	8.0719	10.8245	9.9778	0.1292	9.5011	10.4655	8.4906	0.0763
12*C*	102.6283	155.1849	0.1208	0.9263	78.2369	121.2969	3.6887	0.3607
13*O*	531.9620	541.0139	-1.1595	0.3818	633.1513	674.8552	-1.1001	0.7100
14*O*	175.376	224.1642	2.1845	0.3295	109.8752	181.9736	4.8283	0.3349
15*H*	12.4561	12.4636	5.6760	0.0079	10.1192	10.7197	7.4813	0.0639
16*H*	32.0679	35.8250	0.8771	0.2998	30.1558	31.0488	1.2931	0.1289
	$MoO_4^{2-}GLY(HF)$				$MoO_4^{2-}GLY(B3LYP)$			
	CSA	CSA_a	δ	$\Delta\eta$	*CSA*	CSA_a	δ	$\Delta\eta$
1*Mo*	162.8866	169.1015	18.0545	0.0241	93.0968	102.9268	26.8526	0.0283
2*O*	389.2010	422.6124	-2.4022	-1.8223	198.8352	205.6456	-4.9094	-0.1571
3*O*	640.1266	735.4421	-3.1489	-0.8528	380.5808	484.1840	-5.1913	-0.4269
4*O*	428.9794	495.6864	-2.4438	-2.2593	308.1292	366.0832	-3.9038	-0.5837
5*O*	748.7396	788.5740	-3.1691	-0.4896	507.6516	553.9372	-4.4389	-0.3101
6*N*	47.7320	48.6170	14.1933	0.0207	72.0636	75.5462	8.0175	0.0544
7*C*	28.2168	29.1112	15.7872	0.0247	26.9280	30.1563	14.3962	0.0533
8*H*	21.6592	21.6937	2.1856	0.0234	20.2564	20.3343	2.4120	0.0345
9*H*	23.8317	24.2554	1.9371	0.0833	22.8486	23.5348	1.9714	0.1077
10*H*	10.6694	12.5774	6.0212	0.1348	12.0410	14.8928	4.7401	0.1870
11*H*	6.6498	7.3864	12.6235	0.0573	5.2609	5.8498	15.7709	0.0474
12*C*	103.5582	145.2982	0.1280	0.8010	62.8990	112.5512	0.9796	0.8626
13*O*	262.4334	364.7733	0.4158	-0.8602	350.8306	357.5092	-0.7724	0.2776
14*O*	159.7852	210.6636	2.6114	0.3227	183.3041	201.9047	1.4535	0.2316
15*H*	13.5074	13.5108	5.1720	0.0054	8.7029	8.7512	8.7819	0.0170
16*H*	14.3093	14.4873	5.2951	0.0370	11.6152	11.8416	0.2008	0.0079

Table 5: The hybridizing coefficient of all bonds of, CrO_4^{-2} and MoO_4^{-2} complexes, calculated by NBO method at the levels of HF/6-31G(d) and B3LYP/6-31G(d).

Bond	$HF(CrO_4^{2-})$	$B3LYP(CrO_4^{2-})$
Cr_1-O_2	$\sigma = 0.5587(sp^{0.01}d^{3.30})_{Cr_1} + 0.8294(sp^{7.09}d^{0.02})_{O_2}$	$\sigma = 0.4989(sp^{0.31}d^{2.30})_{Cr_1} + 0.8666(sp^{7.46}d^{0.02})_{O_2}$
		$\pi = 0.3764(p^{6.73}d^{23.14})_{Cr_1} + 0.9265(p)_{O_2}$
Cr_1-O_3	$\sigma = 0.5587(sp^{0.01}d^{3.30}f^{0.02})_{Cr_1} + 0.8294(sp^{7.09}d^{0.02}$	
Cr_1-O_4	$\sigma = 0.5514(sp^{0.06}d^{3.49}f^{0.01})_{Cr_1} + 0.8342(sp^{7.46}d^{0.02}$	$\sigma = 0.5514(sp^{0.06}d^{3.49}f^{0.01})_{Cr_1} + 0.8342(sp^{7.46}d^{0.02})_{O_4}$
		$\pi = 0.3871(sp^{5.60}d^{22.13}f^{0.33})_{Cr_1} + 0.9220(p)_{O_4}$
		$\pi = 0.3724(sp^{9.26}d^{26.47}f^{0.53})_{Cr_1} + 0.9281(p)_{O_4}$
Cr_1-O_5	$\sigma = 0.5587(sp^{0.01}d^{3.03}f^{0.02})_{Cr_1} + 0.8294(sp^{7.09}d^{0.02}$	$\sigma = 0.5166(sp^{0.18}d^{2.35}f^{0.02})_{Cr_1} + 0.8562(sp^{7.46}d^{0.02})_{O_5}$
		$\pi = 0.3871(sp^{5.62}d^{22.15}f^{0.33})_{Cr_1} + 0.9220(p)_{O_5}$
	$HF(MoO_4^{2-})$	$B3LYP(MoO_4^{2-})$
Mo_1-O_2	$\sigma = 0.408(sp^{0.21}d^{2.79})_{Mo_1} + 0.9129(sp^{2.81}d^{0.01})_{O_2}$	$\sigma = 0.4501(sp^{0.08}d^{2.92})_{Mo_1} + 0.8930(sp^{3.80}d^{0.01})_{O_2}$
	$\pi = 0.3181(p^{1.00}d^{5.07})_{Mo_1} + 0.9481(p)_{O_2}$	$\pi = 0.3266(pd^{2.65})_{Mo_1} + 0.9452(p)_{O_2}$
		$\pi = 0.3605(pd^{2.61})_{Mo_1} + 0.9328(p)_{O_2}$
Mo_1-O_3	$\sigma = 0.3928(sp^{0.03}d^{2.79})_{Mo_1} + 0.9196(sp^{2.81}d^{0.01})_{O_3}$	$\sigma = 0.4290(sp^{0.20}d^{2.80})_{Mo_1} + 0.9033(sp^{3.80}d^{0.03})_{O_3}$
		$\pi = 0.3298(pd^{2.72})_{Mo_1} + 0.9440(p)_{O_3}$
Mo_1-O_4	$\sigma = 0.4460(sp^{0.03}d^{2.97})_{Mo_1} + 0.8950(sp^{2.81}d^{0.01})_{O_4}$	$\sigma = 0.4135(sp^{0.29}d^{2.71})_{Mo_1} + 0.9105(sp^{3.80}d^{0.01})_{O_4}$
	$\pi = 0.3248(p\,d^{5.19})_{Mo_1} + 0.9458(p)_{O_4}$	
	$\pi = 0.3187(pd^{4.75})_{Mo_1} + 0.9478(p)_{O_4}$	
Mo_1-O_5	$\sigma = 0.4209(spd^{2.85})_{Mo_1} + 0.9071(sp^{2.81}d^{0.01})_{O_5}$	$\sigma = 0.4301(sp^{0.20}d^{2.80})_{Mo_1} + 0.9028(sp^{3.80}d^{0.01})_{O_5}$
	$\pi = 0.3248(pd^{5.19})_{Mo_1} + 0.9458(p)_{O_5}$	$\pi = 0.2948(pd^{1.95})_{Mo_1} + 0.9556(p^{1.00})_{O_5}$
		$\pi = 0.3600(pd^{3.67})_{Mo_1} + 0.9330(p)_{O_5}$

Table 6: The hybridizing coefficient of all bonds of, $CrO_4^{-2}GLY^{+1}$ and $MoO_4^{-2}GLY^{+1}$ complexes, calculated by NBO method at the levels of HF/6-31G(d) and B3LYP/6-31G(d)

Bond	*HF*($CrO_4^{2-}GLY$)	*B3LYP*($CrO_4^{2-}GLY$)
Cr_1-O_2	$\sigma = 0.4840(sp^{0.23}d)_{Cr_1} + 0.8751(sp^{4.28}d^{0.01})_{O_2}$	$\sigma = 0.5243(sp^{0.01}d^{2.67})_{Cr_1} + 0.8515(sp^{5.37}d^{0.01})_{O_2}$
Cr_1-O_3	$\sigma = 0.5679(sp^{0.02}d^{4.99})_{Cr_1} + 0.8231(sp^{5.34}d^{0.01})_{O_3}$	$\sigma = 0.5754(sp^{0.01}d^{3.84})_{Cr_1} + 0.8179(sp^{5.22}d^{0.01})_{O_3}$
	$\pi = 0.4560(sp^{0.26}d^{4.99})_{Cr_1} + 0.8900(sp^{31.82}d^{0.05})_{O_3}$	$\pi = 0.5278(p^{0.01}d^{99.99})_{Cr_1} + 0.8494(p^{1.00})_{O_3}$
	$\pi = 0.3926(sp^{1.00}d^{5.04})_{Cr_1} + 0.9197(sp^{1.00})_{O_3}$	$\pi = 0.5159(sp^{2.21}d^{99.99})_{Cr_1} + 0.8566(sp^{99.99}d^{0.65})_{O_3}$
Cr_1-O_4	$\sigma = 0.5507(sp^{0.01}d^{3.26})_{Cr_1} + 0.8347(sp^{4.24}d^{0.01})_{O_4}$	$\sigma = 0.5386(sp^{0.01}d^{3.11})_{Cr_1} + 0.8425(sp^{5.32}d^{0.01})_{O_4}$
	$\pi = 0.3861(sp^{99.99}d^{99.99})_{O_3} + 0.9225(sp^{99.99}d^{13.80})_{O_4}$	
Cr_1-O_5	$\sigma = 0.4869(sp^{0.23}d^{2.55})_{Cr_1} + 0.8735(sp^{4.28}d^{0.01})_{O_5}$	$\sigma = 0.5261(sp^{0.01}d^{2.64})_{Cr_1} + 0.8504(sp^{5.35}d^{0.01})_{O_5}$
N_6-C_7	$\sigma = 0.7933(sp^{2.80}d^{0.01})_{N_6} + 0.6089(sp^{3.43}d^{0.01})_{C_7}$	$\sigma = 0.7908(sp^{2.91})_{N_6} + 0.6121(sp^{3.56})_{C_7}$
N_6-H_8	$\sigma = 0.8342(sp^{3.5}d^{0.01})_{N_6} + 0.5515(s)_{H_8}$	$\sigma = 0.8350(sp^{3.44})_{N_6} + 0.5502(s)_{H_8}$
N_6-H_9	$\sigma = 0.4795(sp^{2.90}d^{0.01})_{N_6} + 0.4759(s)_{H_9}$	$\sigma = 0.8749(sp^{2.86})_{N_6} + 0.4843(s)_{H_9}$
N_6-H_{16}	$\sigma = 0.8811(sp^{2.85}d^{0.01})_{N_6} + 0.4730(s)_{H_{16}}$	$\sigma = 0.8758(sp^{2.85})_{N_6} + 0.4826(s)_{H_{16}}$
C_7-H_{10}	$\sigma = 0.8152(sp^{2.63})_{C_7} + 0.5792(s)_{H_{10}}$	$\sigma = 0.8274(sp^{2.68})_{C_7} + 0.5616(s)_{H_{10}}$
C_7-H_{11}	$\sigma = 0.7775(sp^{3.05}d^{0.01})_{C_7} + 0.6289(s)_{H_{11}}$	$\sigma = 0.7829(sp^{3.04})_{C_7} + 0.6221(s)_{H_{11}}$
C_7-C_{12}	$\sigma = 0.7104(sp^{2.93}d^{0.01})_{C_7} + 0.7038(sp^{1.62})_{C_{12}}$	$\sigma = 0.7107(sp^{2.80})_{C_7} + 0.7035(sp^{1.54})_{C_{12}}$
$C_{12}-O_{13}$	$\sigma = 0.5813(sp^{1.90})_{C_{12}} + 0.8137(sp^{1.25}d^{0.01})_{O_{13}}$	$\sigma = 0.5860(sp^{2.10})_{C_{12}} + 0.8103(sp^{1.56}d^{0.01})_{O_{13}}$
	$\pi = 0.5132(sp^{99.99}d^{2.38})_{C_{12}} + 0.8582(sp^{99.99}d^{3.88})_{O_{13}}$	$\pi = 0.5468(sp^{51.13}d^{0.01})_{C_{12}} + 0.8373(sp^{44.59}d^{015})_{O_{13}}$
$C_{12}-O_{14}$	$\sigma = 0.5528(sp^{2.62}d^{0.01})_{C_{12}} + 0.8333(sp^{1.81})_{O_{14}}$	$\sigma = 0.5608(sp^{2.73}d^{0.01})_{C_{12}} + 0.8280(sp^{2.01})_{O_{14}}$
$O_{14}-H_{15}$	$\sigma = 0.8652(sp^{3.29}d^{0.01})_{O_{14}} + 0.5014(s)_{H_{15}}$	$\sigma = 0.8624(sp^{3.73}d^{0.01})_{O_{14}} + 0.5063(s)_{H_{15}}$
	HF($MoO_4^{2-}GLY$)	*B3LYP*(MoO_4^{2} *GLY*)
Mo_1-O_2	$\sigma = 0.3770(sp^{0.37}d^{2.47})_{Mo_1} + 0.9262(sp^{2.57}d^{0.01})_{O_2}$	$\sigma = 0.3810(sp^{0.44}d^{2.70})_{Mo_1} + 0.9246(sp^{3.53})_{O_2}$
Mo_1-O_3	$\sigma = 0.3704(sp^{0.54}d^{3.51})_{Mo_1} + 0.9289(sp^{3.48}d^{0.01})_{O_3}$	$\sigma = 0.4180(sp^{0.32}d^{3.02})_{Mo_1} + 0.9082(sp^{3.85})_{O_3}$
	$\pi = 0.2896(sp^{2.61}d^{12.88})_{Mo_1} + 0.9571(sp^{18.70}d^{0.02})_{O_3}$	$\pi = 0.3606(sp^{7.55}d^{32.99})_{Mo_1} + 0.9327(sp^{99.99}d^{0.99})_{O_3}$
	$\pi = 0.2702(sp^{8.86}d^{32.76})_{Mo_1} + 0.9628(sp^{99.99}d^{2.94})_{O_3}$	
Mo_1-O_4	$\sigma = 0.4110(sp^{0.27}d^{3.23})_{Mo_1} + 0.9116(sp^{2.92}d^{0.01})_{O_4}$	$\sigma = 0.4412(sp^{0.31}d^{3.57})_{Mo_1} + 0.8974(sp^{4.00}d^{0.01})_{O_4}$
	$\pi = 0.3432(sp^{41.12}d^{99.99})_{Mo_1} + 0.9393(sp^{99.99}d^{0.6})_{O_4}$	$\pi = 0.4135(sp^{11.80}d^{54.15})_{Mo_1} + 0.9105(sp^{92.88}d^{0.10})_{O_4}$
Mo_1-O_5	$\sigma = 0.4492(sp^{0.18}d^{2.85})_{Mo_1} + 0.8934(sp^{2.81}d^{0.01})_{O_5}$	$\sigma = 0.5008(sp^{0.02}d^{2.5})_{Mo_1} + 0.8656(sp^{3.51}d^{0.01})_{O_5}$
	$\pi = 0.3113(sp^{28.79}d^{92.25})_{Mo_1} + 0.9503(sp^{99.99}d^{3.50})_{O_5}$	$\pi = 0.3825(sp^{99.99}d^{99.99})_{Mo_1} + 0.9240(sp^{1.00})_{O_5}$
	$\pi = 0.3397(sp^{64.88}d^{99.99})_{Mo_1} + 0.9405(p)_{O_5}$	$\pi = 0.4198(sp^{99.99}d^{99.99})_{Mo_1} + 0.9076(sp^{99.99}d^{0.82})_{O_5}$
N_6-C_7	$\sigma = 0.8029(sp^{2.84}d^{0.01})_{N_6} + 0.5961(sp^{3.86}d^{0.01})_{C_7}$	$\sigma = 0.8019(sp^{3.02})_{N_6} + 0.5974(sp^{4.16}d^{0.01})_{C_7}$
N_6-H_8	$\sigma = 0.8367(sp^{3.38}d^{0.01})_{N_6} + 0.5476(s)_{H_8}$	$\sigma = 0.8389(sp^{3.27})_{N_6} + 0.5443(s)_{H_8}$
N_6-H_9	$\sigma = 0.8757(sp^{2.92}d^{0.01})_{N_6} + 0.4829(s)_{H_9}$	$\sigma = 0.8696(sp^{2.95})_{N_6} + 0.4938(s)_{H_9}$
N_6-H_{16}	$\sigma = 0.8715(sp^{2.88}d^{0.01})_{N_6} + 0.4903(s)_{H_{16}}$	$\sigma = 0.8682(sp^{2.78})_{N_6} + 0.4963(s)_{H_{16}}$
C_7-H_{10}	$\sigma = 0.7749(sp^{3.12}d^{0.01})_{C_7} + 0.6321(s)_{H_{10}}$	$\sigma = 0.7823(sp^{3.10})_{C_7} + 0.6229(s)_{H_{10}}$
C_7-H_{11}	$\sigma = 0.8034(sp^{2.43}d^{0.01})_{C_7} + 0.5955(s)_{H_{11}}$	$\sigma = 0.8040(sp^{2.46})_{C_7} + 0.5946(s)_{H_{11}}$
C_7-C_{12}	$\sigma = 0.7235(sp^{2.77}d^{0.01})_{C_7} + 0.6904(sp^{1.74})_{C_{12}}$	$\sigma = 0.7288(sp^{2.65})_{C_7} + 0.6847(sp^{1.79})_{C_{12}}$

$C_{12}-O_{13}$	$\sigma = 0.5781(sp^{1.92})_{C_{12}} + 0.8160(sp^{3.24}d^{0.01})_{O_{13}}$	$\sigma = 0.5858(sp^{1.92})_{C_{12}} + 0.8105(sp^{1.48}d^{0.01})_{O_{13}}$
	$\pi = 0.4927(sp^{99.99}d^{16.36})_{C_{12}} + 0.8702(sp^{99.99}d^{1.18})_{O_{13}}$	$\pi = 0.5016(sp^{99.99}d^{0.49})_{C_{12}} + 0.8651(sp^{99.99}d^{0.38})_{O_{13}}$
$C_{12}-O_{14}$	$\sigma = 0.5562(sp^{2.39}d^{0.01})_{C_{12}} + 0.8311(sp^{1.67}d^{0.01})_{O_{14}}$	$\sigma = 0.5662(sp^{2.40}d^{0.01})_{C_{12}} + 0.8243(sp^{1.89})_{O_{14}}$
$O_{14}-H_{15}$	$\sigma = 0.8635(sp^{3.51}d^{0.02})_{O_{14}} + 0.5044(s)_{H_{15}}$	$\sigma = 0.8583(sp^{4.24}d^{0.01})_{O_{14}} + 0.5131(s)_{H_{15}}$

Table 7: The contribution of (p&d) orbital in (σ & π) bonds of, and $CrO_4^{-2}GLY^{+1}$, $MoO_4^{-2}GLY^{+1}$ complexes, calculated by NBO method at the levels of HF/6-31G (d) and B3LYP/6-31G(d).

bonds	$CrO_4^{2-}GLY(HF)$				$CrO_4^{2-}GLY(B3LYP)$			
	σ		π		σ		π	
	p	*d*	*p*	*d*	*p*	*d*	*p*	*d*
$Cr-O_2$	2.83	0.3625	-	-	0.01	1.02	-	-
$Cr-O_3$	3.17	2.043	21.13 1.00	1.72 1.51	3.068	1.59	0.6206 63.24	38.32 37.99
$Cr-O_4$	2.56	1.302	99.99	39.23	3.24	1.22	-	-
$Cr-O_5$	2.83	0.8475	-	-	3.31	1.02	-	-
N_6-C_7	3.07	0.01	-	-	3.19	0.00	-	-
N_6-H_8	3.5	6.02e-3	-	-	2.074	0.00	-	-
N_6-H_9	2.90	5.02e-3	-	-	1.84	0.00	-	-
N_6-H_{16}	2.85	6.51e-3	-	-	1.84	0.00	-	-
C_7-H_{10}	2.63	0.00	-	-	0.5957	0.00	-	-
C_7-H_{11}	3.05	5.54e-3	-	-	1.596	0.00	-	-
C_7-C_{12}	2.27	5.02e-3	-	-	2.17	0.00	-	-
$C_{12}-O_{13}$	1.52	5.83e-3	99.99	3.32	1.787	5.80e-3	47.17	0.0947
$C_{12}-O_{14}$	2.12	3.99e-3	-	-	2.32	4.04e-3	-	-
$O_{14}-H_{15}$	3.29	6.33e-3	-	-	2.35	6.30e-3	-	-
bonds	$MoO_4^{2-}GLY(HF)$				$MoO_4^{2-}GLY(B3LYP)$			
	σ		π		σ		π	
	p	*d*	*p*	*d*	*p*	*d*	*p*	*d*
$Mo-O_2$	1.93	0.7216	-	-	2.63	0.7879	-	-
$Mo-O_3$	2.64	1.01	14.96 80.02	3.01 9.47	2.74	0.9519	74.22	9.26
$Mo-O_4$	2.10	1.01	84.24	28.29	2.78	1.183	2.78	16.9185
$Mo-O_5$	1.93	0.9602	82.42 17.95	25.40 26.53	2.23	0.9226	29.98 99.99	29.27 32.18
N_6-C_7	3.27	0.01	-	-	3.51	4.27e-3	-	-
N_6-H_8	3.38	6.04e-3	-	-	1.98	0.00	-	-
N_6-H_9	2.92	6.45e-3	-	-	1.88	0.00	-	-
N_6-H_{16}	2.88	3.40e-3	-	-	1.77	0.00	-	-
C_7-H_{10}	3.12	5.51e-3	-	-	1.73	0.00	-	-
C_7-H_{11}	2.47	5.74e-3	-	-	1.41	0.00	-	-
C_7-C_{12}	2.27	5.12e-3	-	-	1.37	0.00	-	-
$C_{12}-O_{13}$	1.52	5.85e-3	99.99	6.67	1.62	5.81e-3	99.99	0.4204
$C_{12}-O_{14}$	1.95	0.01	-	-	2.10	0.00	-	-
$O_{14}-H_{15}$	3.51	0.012	-	-	2.56	0.00	-	-

REFERENCES

1. Some metals and metallic compounds. Lyon, international agency for research on cancer, **(1980)**(IARC monographs on the evaluation of carcinogenic risk of chemicals to humans, vol. 23.
2. Wigand, H.J.ETAL.Disposition of intratracheally administered. Chromium ^{III} and chromium ^{VI} in rabbits. Toxicology letters, 22, 273-276(**1984**).
3. Cotton, FA and Wilkinson, G.(**1980**) Advanced organic chemistry. A comprehensive text, 4th Ed. New York: John Wiley and Sons, Inc., pp. 719-736.
4. A.Pechova, A.Podhorsky, E & etal.Acta Vet. Brno (**2002**), 71:9-81
5. Royj.Irmin "Environmental contaminants Encyclopedia Chromium (*VI*) (Hexavalent Chromium) energy July 1, (**1997**).
6. D.L.Kepert, Chromium, Molybdenum, Tungsten, Chap.4 in The Early Transition Metals, pp.255-374, Academic Press, London, (**1972**).
7. Environ.sci.Technol., (**2002**), 36, 1124-1129.
8. WHO Regional Office for Europe, Copenhagen, Denmark, (**2000**).
9. Renate Krupa, marcin stanczak and Zofia Walter, Z.Naturforsch 57c, 951-953(**2002**).
10. A.Pechova, A.Pdhorsky, E.Lokajova, L.Pavlta, j.illek, ACTA.VET.BRNO (**2002**), 71; 9-18.
11. M.Monajjemi, R.Ghiasi, H.Passdar, F.Mollaamin, S.Ketabi, F.Asaddian, B.Chahkandi, and M.Karimkhani, Internet electronic Journal of Molecular Design (**2003**), 2.
12. B.R.Harvey, R.D.Ibbett, K.J.Williams and M.B.Lovett, LOWESTOFT (**1991**).
13. Lars Johnsson, NF J Seminar no.370, 15-17 August (**2005**).
14. W.G.KlEMPER and W.SHUM, Synthesis and interconversion of the isomeric α – and $\beta - Mo_8O_{26}$ ions, j.Am.Chem. Soc.98, 8291-3(**1976**).
15. R. D. Peacock, Technetium, chap. 38 in Comprehensive Inorganic Chemistry, Vol. 3,pp. 877-903, Pergamon press, Oxford, (**1973**).
16. Todd M.Alam int.J.Mol sci.(**2002**), 3,888-906.
17. Jiri czernek, Radovan Fiala, and Vladimir Sklenar, Journal of Magnetic Resonance 145,142-146 (**2000**).
18. M.Monajjemi et al J.Phys. &Theo.Chem.I.A.U Iran Vol.1, NO.4, Winter (**2000**).
19. P. Hohenberg and W. Kohn, *Phys. Rev.* 136, B864 (**1964**).
20. W. Kohn and L. J. Sham, *Phys. Rev.* 140, A1133 (**1965**).
21. J. C. Slater, *Quantum Theory of Molecular and Solids, Vol. 4: The Self-Consistent Field for Molecular and Solids* (McGraw-Hill, New York, **1974**).
22. J. A. Pople, P. M. W. Gill, and B. G. Johnson, *Chem. Phys. Lett.* 199, 557 (**1992**).
23. A. D. Becke, *J. Chem. Phys.* 98, 5648 (**1993**).
24. M. J. Frisch, M. Head-Gordon, and J. A. Pople, *J. Chem. Phys.* 141, 189 (**1990**).
25. M. Head-Gordon, J. A. Pople, and M. J. Frisch, *Chem. Phys. Lett.* 153, 503 (**1988**).
26. M. J. Frisch, M. Head-Gordon, and J. A. Pople, *Chem. Phys. Lett.* 166, 275 (**1990**).
27. M. J. Frisch, M. Head-Gordon, and J. A. Pople, *Chem. Phys. Lett.* 166, 281 (**1990**).
28. J. Almloff, K. Korsell, and K. Faegri Jr., *J. Comp. Chem.* **3**, 385 (**1982**).
29. M. Head-Gordon and T. Head-Gordon, *Chem. Phys. Lett.* 220, 122 (**1994**).
30. M. Head-Gordon and J. A. Pople, *J. Chem. Phys.* 89, 5777 (**1988**).
31. P. M. W. Gill, *Adv. Quant. Chem.* 25, 143 (**1994**).
32. P. R. Taylor, *Int. J. Quant. Chem.* 31, 521 (**1987**).
33. J. Gauss, *J. Chem. Phys.* 99, 3629 (**1993**).
34. J. Gauss, PCCP Phys. Chem. *Chem. Phys.* 99, 1001 (**1995**).
35. J. R. Cheeseman, G. W. Trucks, and M. J. Frisch, in prep. (**2003**).
36. 1. RJ Doist, DHP Streeton, JM Freiberg and AJ Schneider; Trace Elements in Human Health and Disease;, Academic Press, Inc, ed, AS Prasad, New York, Vol II, pp 79-104, (**1976**).
37. Kaufman, DB, DiNicola, W, McIntosh, R. Acute potassium dichromate poisoning:
Treated by peritoneal dialysis. *Am. J. Dis. Child.* 119, 374-376 (**1970**).