Supplementary Material (ESI) for Physical Chemistry Chemical Physics

The critical reevaluation of the aromatic/antiaromatic nature of $Ti_3(CO)_3$: A missed opportunity?

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Table S-1. The stability of the optimized geometries of different species at BP86/6-311+G(d) and LSDA/6-311+G(d) levels.

Molecule	BP86/6-311+G(d)	LSDA/6-311+G(d)
$[Sc_3(CO)_3]^+$	Instable	Stable
$Ti_3(CO)_3$	Stable	Stable
$[V_3(CO)_3]^+$	Stable	Stable
$[Cr_3(CO)_3]^{2+}$	Instable	Instable
$Ni_3(CO)_3$	Stable	Stable
$[Cu_3(CO)_3]^-$	Stable	Stable

Table S-2. $NICS_{zz}$ values of $Ti_3(CO)_3$ at various distances above the ring plane of $Ti_3(CO)_3$ at four DFT levels with three basis sets.

$Ti_3(CO)_3$		6-311+G(d)	6-311+G(2df)	6-311+G(3d2f)
LSDA	$NICS(0)_{zz}$	-120.61	-120.09	-119.78
	$NICS(0.5)_{zz}$	-81.37	-81.19	-80.81
	$NICS(1)_{zz}$	-20.83	-20.96	-20.76
BP86	$NICS(0)_{zz}$	-117.89	-117.22	-116.76
	$NICS(0.5)_{zz}$	-80.31	-80.02	-79.06
	$NICS(1)_{zz}$	-20.77	-20.82	-20.64
MPWPW91	$NICS(0)_{zz}$	-132.18	-115.73	-115.13
	$NICS(0.5)_{zz}$	-87.75	-79.0	-78.48
	$NICS(1)_{zz}$	-15.03	-20.48	-20.26
B3LYP	$NICS(0)_{zz}$	-140.85	-138.47	-137.86
	$NICS(0.5)_{zz}$	-94.58	-93.04	-92.48
	$NICS(1)_{zz}$	-18.43	-18.14	-17.91

Table S-3. $NICS_{zz}$ values of metal carbonyls at various distances above the ring planes of the molecules.

Metal Carbonyls		$V_3(CO)_3^+$	$Ni_3(CO)_3$	$Cu_3(CO)_3^-$
LSDA 6-311+G(d)	$NICS(0)_{zz}$	-238.41	-12.09	-35.82
	$NICS(0.5)_{zz}$	-132.63	-9.08	-32.28
	$NICS(1)_{zz}$	-7.72	-4.81	-26.20
BP86 6-311+G(d)	$NICS(0)_{zz}$	-239.76	-13.99	-33.38
	$NICS(0.5)_{zz}$	-135.69	-10.57	-30.09
	$NICS(1)_{zz}$	-8.26	-5.40	-24.45

Table S-4. Detailed dissected CMO-NICS analysis of $Ti_3(CO)_3$: contribution of diamagnetic shielding (σ^{dia}) and contributions of gauge (σ^{gauge}), occupied to occupied ($\sigma^{para,occ,occ}$) and occupied to virtual ($\sigma^{para,occ-vir}$) components of paramagnetic shielding. The main contribution of occupied to virtual component (Occ→Vir) for each canonical MO and the total contribution of each canonical MO ($NICS_{MO}$) are separately presented.

Orbitals	σ^{dia}	σ^{gauge}	$\sigma^{para,occ,occ}$	$\sigma^{para,occ-vir}$	Occ→Vir	$NICS_{MO}$
49	-5.8	2.4	-1.8	-8.8×2 -10.4×2 3.0	49→61, 62 49→63, 64 49→other Vir	-40.8
50	-5.8	2.4	-1.8	-8.8×2 -10.4×2 3.0	50→61, 62 50→63, 64 50→other Vir	-40.8
51	-6.2	-4.9	0.0	23.0 2.54	51→65 51→other Vir	14.4
52	-0.7	-3.2	0.0	10.1 1.9×2 0.3	52→57 52→63, 64 52→other Vir	10.4
53	-0.9	-2.3	0.0	-4.7×2 2.7	53→61, 62 53→other Vir	-9.8
54	-0.9	-2.3	0.0	-4.7×2 2.7	54→61, 62 54→other Vir	-9.8

Figure S-1. The energy diagram of some of the highest occupied MO of $Ti_3(CO)_3$

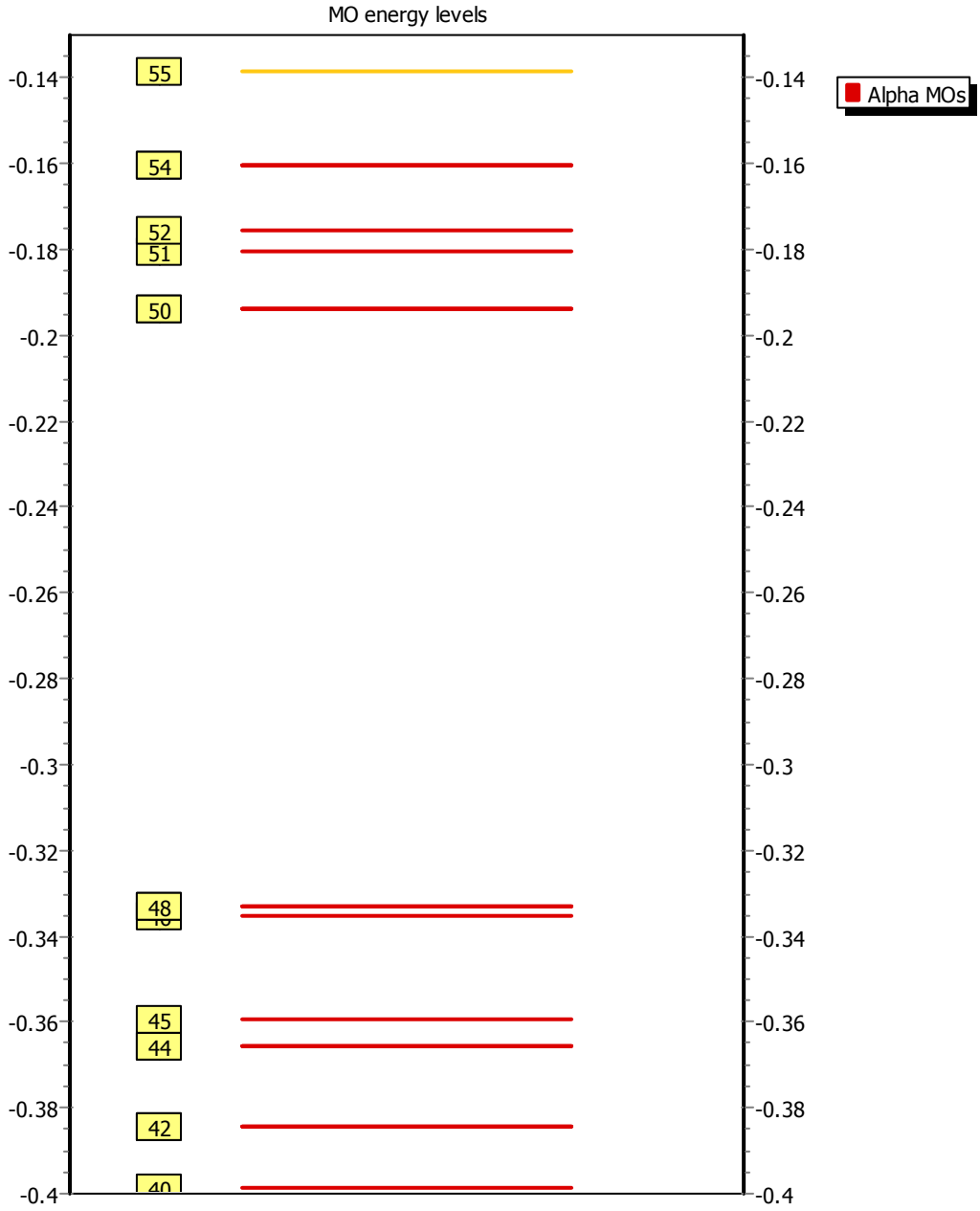
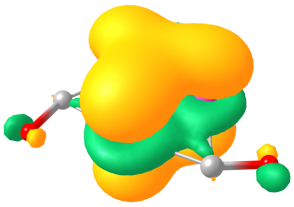
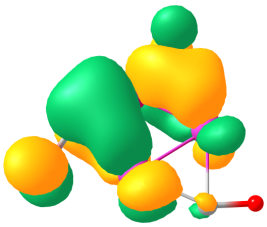


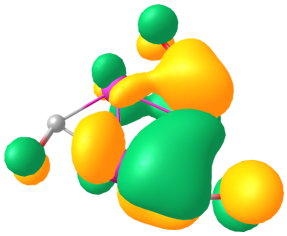
Figure S-2. The morphology of the seven highest occupied MO of $V_3(CO)_3^+$



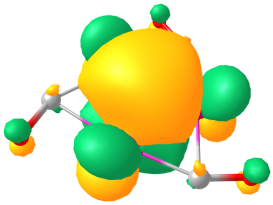
MO 55



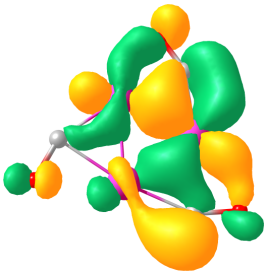
MO 54



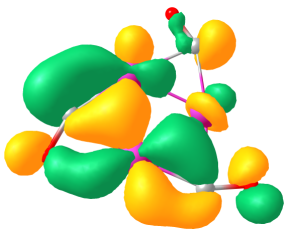
MO 53



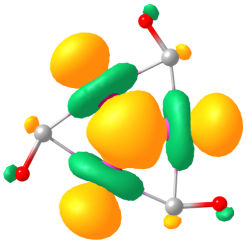
MO 52



MO 51

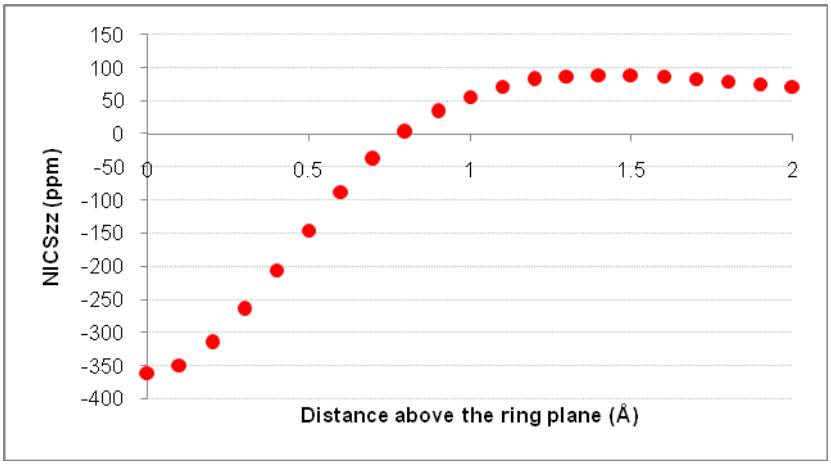


MO 50

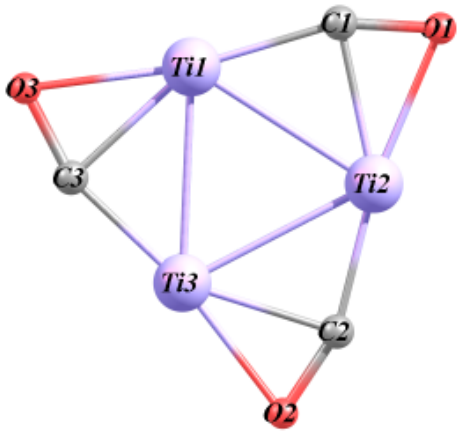


MO 49

Figure S-3. NICS scan plot of V_3^+, this is evidently similar to that of $V_3(CO)_3^+$ and V_3^-.



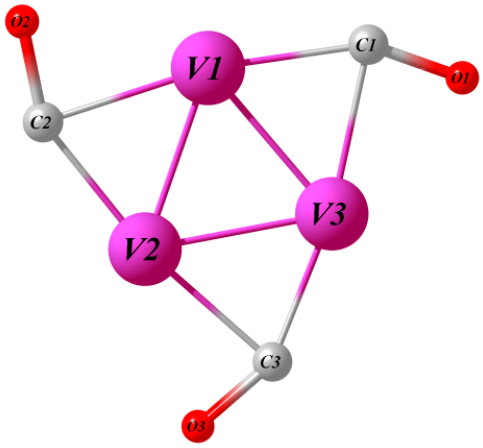
Scheme S-1. QTAIM analysis: The detailed results for the four local minima (*E* stands for energy, *Q* for charge and *λ* for the localization index)



Atoms	**E**	**Q**	**λ**
Ti_1	-849.46216	1.140	18.7
Ti_2	-849.46227	1.140	18.7
Ti_3	-849.46195	1.140	18.7
C_1	-37.73682	-0.036	4.3
C_2	-37.73618	-0.034	4.3
C_3	-37.73707	-0.037	4.3
O_1	-75.73840	-1.102	8.0
O_2	-75.73849	-1.102	8.0
O_3	-75.73849`	-1.101	8.0

$E_{Tot} - \Sigma E_{\Omega} = 2.4$ kcal mol^{-1} **$Q_{Tot} - \Sigma Q_{\Omega} = -0.0075$ e**

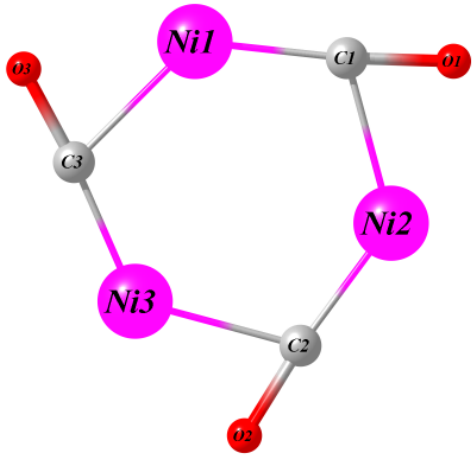
Delocalization index	**δ (Ti_1, x)**	**δ (C_1, x)**
Ti_2	0.82	
Ti_3	0.82	
C_1	1.14	
C_2	0.07	0.07
C_3	0.74	0.07
O_1	0.19	1.33
O_2	0.02	0.02
O_3	0.51	0.06



Atoms	**E**	**Q**	**λ**
V_1	-944.15642	0.877	19.4
V_2	-944.00785	0.881	19.3
V_3	-944.00692	0.879	19.3
C_1	-37.59219	0.456	3. 9
C_2	-37.59206	0.458	3.9
C_3	-37.59245	0.456	3.9
O_1	-75.81305	-1.004	7.9
O_2	-75.81291	-1.004	7.9
O_3	-75.81311	-1.004	7.9

$E_{Tot} - \Sigma E_{\Omega} = 91.4$ kcal mol^{-1} **$Q_{Tot} - \Sigma Q_{\Omega} = 0.0030$ e**

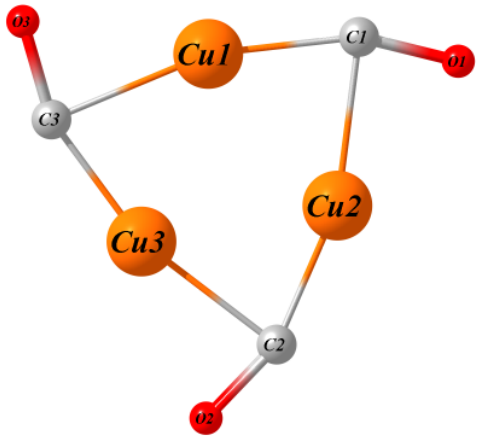
Delocalization index	**δ (V_1, x)**	**δ (C_1, x)**
V_2	1.64	
V_3	1.64	
C_1	0.95	
C_2	0.60	0.04
C_3	0.09	0.04
O_1	0.18	1.52
O_2	0.39	0.03
O_3	0.04	0.02



Atoms	**E**	**Q**	**λ**
Ni_1	-1508.58718	0.466	25.9
Ni_2	-1508.58860	0.466	25.9
Ni_3	-1508.58909	0.466	25.9
C_1	-37.53540	0.575	3.7
C_2	-37.53571	0.574	3.7
C_3	-37.53583	0.574	3.7
O_1	-75.78928	-1.040	7.9
O_2	-75.78923	-1.040	7.9
O_3	-75.78951	-1.040	7.9

$E_{Tot} - \Sigma E_{\Omega} =$ 22.8 kcal mol^{-1} **$Q_{Tot} - \Sigma Q_{\Omega} =$ -0.0009e**

Delocalization index	**δ (Ni_1, x)**	**δ (C_1, x)**
Ni_2	0.2370	
Ni_3	0.2370	
C_1	1.3119	
C_2	0.0288	0.0168
C_3	0.6343	0.0168
O_1	0.2211	1.4085
O_2	0.0142	0.0034
O_3	0.5808	0.0314



Atoms	**E**	**Q**	**λ**
Cu_1	-1640.86824	0.374	27.1
Cu_2	-1640.86480	0.375	27.1
Cu_3	-1640.86742	0.375	27.1
C_1	-37.51422	0.364	3.9
C_2	-37.51524	0.362	3.9
C_3	-37.51481	0.363	3.9
O_1	-75.72861	-1.071	8.0
O_2	-75.72863	-1.071	8.0
O_3	-75.72862	-1.071	8.0

$E_{Tot} - \Sigma E_{\Omega} = 7.0$ kcal mol^{-1} **$Q_{Tot} - \Sigma Q_{\Omega} = 0.0001$ e**

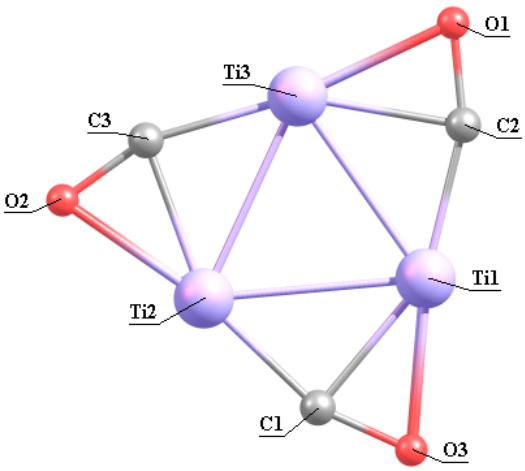
Delocalization index	**δ (Cu_1, x)**	**δ (C_1, x)**
Cu_2	0.38	
Cu_3	0.38	
C_1	1.01	
C_2	0.10	0.12
C_3	0.54	0.12
O_1	0.15	1.44
O_2	0.06	0.06
O3	0.35	0.07

Scheme S-2. Wiberg Bond Index Data at BP86/6-311+G(d) Computational Level

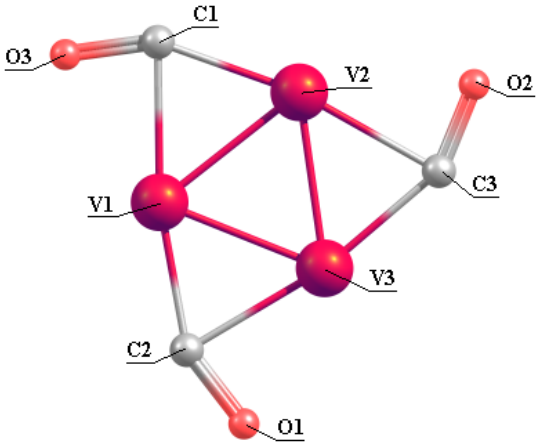
Italic values in parenthesis are bond lengths.

CO
C–O: 2.2999 (*1.140*)

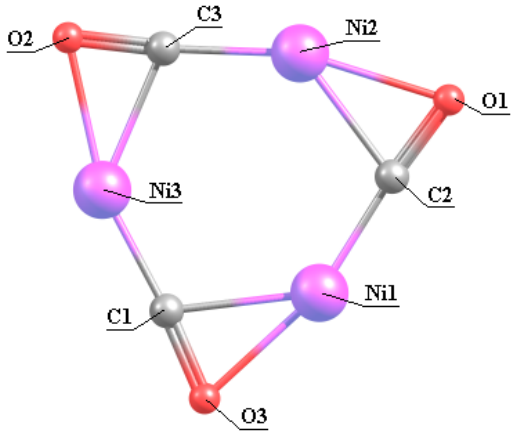
$Ti_3(CO)_3$
Ti(1)–Ti(2): 0.9669 (*2.730*)
Ti(1)–C(1): 0.6895 (*2.062*)
Ti(1)–C(2): 1.1364 (*1.937*)
Ti(1)–O(3): 0.4188 (*2.110*)
C(1)–O(3): 1.4644 (*1.259*)



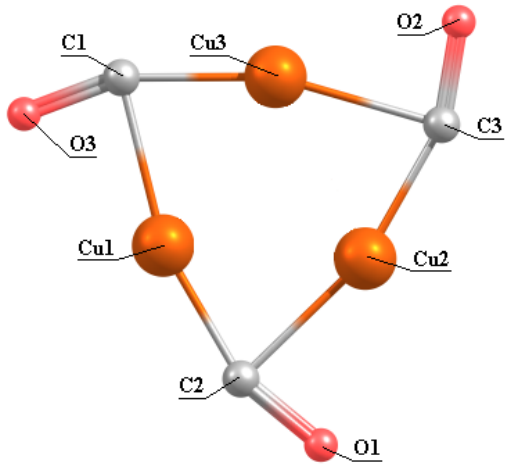
$V_3(CO)_3^+$
V(1)–V(2): 1.7766 (*2.280*)
V(1)–C(1): 0.4898 (*2.055*)
V(1)–C(2): 0.8893 (*1.926*)
V(1)–O(3): 0.2937 (*2.245*)
C(1)–O(3): 1.8671 (*1.196*)



$Ni_3(CO)_3$
Ni(1)–Ni(2): 0.0836 (*3.054*)
Ni(1)–C(1): 0.5095 (*1.954*)
Ni(1)–C(2): 0.8929 (*1.742*)
Ni(1)–O(3): 0.2426 (*1.981*)
C(1)–O(3): 1.7965 (*1.213*)



$Cu_3(CO)_3^-$
Cu(1)–Cu(2): 0.1000 (*2.396*)
Cu(1)–C(1): 0.3373 (*2.045*)
Cu(1)–C(2): 0.5368 (*1.825*)
Cu(1)–O(3): 0.1255 (*2.264*)
C(1)–O(3): 1.6034 (*1.228*)



The Cartesian coordinates of the optimized geometry (BP86/6-311+G(d)) of the species considered in this paper.

$Sc_3(CO)_3^+$

SCANDIUM	21.0	0.000000000	1.904856000	0.000000000
SCANDIUM	21.0	-1.649654000	-0.952428000	0.000000000
SCANDIUM	21.0	1.649654000	-0.952428000	0.000000000
CARBON	6.0	-2.095295000	1.089354000	0.000000000
CARBON	6.0	1.991056000	1.269902000	0.000000000
CARBON	6.0	0.104239000	-2.359256000	0.000000000
OXYGEN	8.0	3.039782000	0.598539000	0.000000000
OXYGEN	8.0	-1.001541000	-2.931797000	0.000000000
OXYGEN	8.0	-2.038241000	2.333259000	0.000000000

$Ti_3(CO)_3$

TITANIUM	22.0	0.000000000	1.576079000	0.000000000
TITANIUM	22.0	-1.364924000	-0.788039000	0.000000000
TITANIUM	22.0	1.364924000	-0.788039000	0.000000000
CARBON	6.0	-1.992451000	1.044369000	0.000000000
CARBON	6.0	1.900675000	1.203329000	0.000000000
CARBON	6.0	0.091776000	-2.247697000	0.000000000
OXYGEN	8.0	2.985240000	0.563111000	0.000000000
OXYGEN	8.0	-1.004951000	-2.866849000	0.000000000
OXYGEN	8.0	-1.980288000	2.303738000	0.000000000

$V_3(CO)_3^+$

CARBON	6.0	-2.036730000	1.045918000	0.000000000
CARBON	6.0	1.924156000	1.240901000	0.000000000
CARBON	6.0	0.112574000	-2.286819000	0.000000000
OXYGEN	8.0	2.964341000	0.650543000	0.000000000
OXYGEN	8.0	-0.918784000	-2.892466000	0.000000000
OXYGEN	8.0	-2.045557000	2.241923000	0.000000000
VANADIUM	23.0	0.000000000	1.315758000	0.000000000
VANADIUM	23.0	-1.139480000	-0.657879000	0.000000000
VANADIUM	23.0	1.139480000	-0.657879000	0.000000000

$Cr_3(CO)_3^{2+}$

CARBON	6.0	2.172580000	0.537520000	0.000000000
CARBON	6.0	-0.620784000	-2.150270000	0.000000000
CARBON	6.0	-1.551796000	1.612749000	0.000000000
OXYGEN	8.0	-1.792043000	-2.320984000	0.000000000
OXYGEN	8.0	-1.114010000	2.712446000	0.000000000
OXYGEN	8.0	2.906052000	-0.391463000	0.000000000
CHROMIUM	24.0	0.502600000	1.280277000	0.000000000
CHROMIUM	24.0	0.857452000	-1.075403000	0.000000000
CHROMIUM	24.0	-1.360053000	-0.204874000	0.000000000

$Ni_3(CO)_3$

CARBON	6.0	-1.726576000	0.848725000	0.000000000
CARBON	6.0	1.598186000	1.070914000	0.000000000
CARBON	6.0	0.128359000	-1.919692000	0.000000000
OXYGEN	8.0	2.746651000	0.680025000	0.000000000
OXYGEN	8.0	-0.784577000	-2.718676000	0.000000000
OXYGEN	8.0	-1.962212000	2.038800000	0.000000000
NICKEL	28.0	-0.000054000	1.762902000	0.000000000
NICKEL	28.0	1.526841000	-0.881597000	0.000000000
NICKEL	28.0	-1.526618000	-0.881400000	0.000000000

$Cu_3(CO)_3^-$

CARBON	6.0	-1.998126000	0.948390000	0.000000000
CARBON	6.0	1.820393000	1.256233000	0.000000000
CARBON	6.0	0.177733000	-2.204623000	0.000000000
OXYGEN	8.0	2.940472000	0.753288000	0.000000000
OXYGEN	8.0	-0.817869000	-2.923168000	0.000000000
OXYGEN	8.0	-2.122603000	2.169880000	0.000000000
COPPER	29.0	0.000000000	1.383258000	0.000000000
COPPER	29.0	1.197937000	-0.691629000	0.000000000
COPPER	29.0	-1.197937000	-0.691629000	0.000000000