

On the structure of $[\text{Al}(\text{DMSO}_2)_3]^{3+}$

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In the memory of Prof. Ing. Ladislav Valko, DrSc. (1930–2013)

Abstract: The most stable $[\text{Al}(\text{DMSO}_2)_3]^{3+}$ complex cation in dimethyl sulfone (DMSO_2 , $(\text{CH}_3)_2\text{SO}_2$) has D_3 symmetry with twofold axes in Al-S lines coincident with the twofold rotation axes of mutually turned DMSO_2 ligands by ca 60°. The central Al atom is hexacoordinated by six O atoms with nearly octahedral coordination. More than one electron is transferred to the Al central atom from DMSO_2 ligands. Weaker and longer S—O, stronger and shorter S—C bonds, lower O—S—O bond angles and greater O—S—C and C—S—C ones in $[\text{Al}(\text{DMSO}_2)_3]^{3+}$ than in free DMSO_2 are implied by weak Al—O bonding.

Keywords: B3LYP, MP2, geometry optimization, electron structure, solvent effect

Introduction

Aluminum is widely used in aircrafts, aerospace, optical and automobile industry due to its very good corrosion resistance and physico-chemical properties. While most aluminium coatings are fabricated by hot-dipping or physical vapour deposition, electrodeposition of aluminium is attracting growing attention since this method operates at a substantially lower temperature and thus offers many advantages such as low cost, simple operation, uniform thickness distribution, and even better control of the microstructure of the deposited layers. The electrodeposited aluminium coatings are also of higher purity and lower porosity, which results in good corrosion protection. The thermal stress in the substrate material may be also avoided since the deposition of aluminum from electrolytic bath usually operates at or near room temperatures (Gálová 1980, Zhao and Van der Noot 1997).

The electrodeposited aluminium coatings could not be obtained in aqueous solutions since hydrogen evolution occurs before the deposition of the metal. There are two main types of media available for the electrodeposition of aluminum (Zhao and Van der Noot 1997), i.e., nonaqueous organic solvents and molten salts. Organic solvents (such as aromatic hydrocarbons and ethers (Gálová 1980, Lehmkühl et al. 1990)) are usually inflammable, volatile, and have relatively low conductivity and narrow electrochemical window. Inorganic molten salts (such as $\text{AlCl}_3/\text{NaCl}/\text{KCl}$ system) operate at relatively high temperatures (above 150 °C) (Fellner et al. 1981), while organic molten salts (known as ionic liquids, such as AlCl_3/N -(1-butyl)pyridinium chloride (Yang 1994) and $\text{AlCl}_3/1$ -methyl-3-ethylimidazolium chloride (Liao et al. 1997)), operate at near room tempera-

tures. Ionic liquids have many unique features such as low vapor pressure, good electrical conductivity and wide electrochemical window, and thus have attracted considerable attention in aluminium electrodeposition and electrorefining over the last years. Nanocrystalline aluminum deposits have been obtained from AlCl_3 -based ionic liquids as well (Zein El Abedin et al. 2005, Endres et al. 2003).

Just as well sulfone-based electrolytes can be used as electrodeposition media of aluminium (Legrand et al. 1995). These electrolytes are cheap and very simple in terms of preparation, and have been reported to obtain the electrodeposited coatings of aluminum over a wide range of temperatures (80–150 °C) (Pereira-Ramos et al. 1986, Legrand et al. 1994, Legrand et al. 1995, Legrand et al. 1996a). $\text{AlCl}_3/\text{dimethyl sulfone}$ (DMSO_2 , $(\text{CH}_3)_2\text{SO}_2$) electrolytes are very attractive due to their relatively high conductivity, good thermal stability and low toxicity.

^{27}Al NMR (Legrand et al. 1995) and Raman analyses (Legrand et al. 1996b) of the $\text{AlCl}_3/\text{DMSO}_2$ mixtures indicate that there are two main soluble aluminium species, namely $[\text{AlCl}_4]^-$ and $[\text{Al}(\text{DMSO}_2)_3]^{3+}$, formed according to the following reaction:



Aluminum can be electrochemically obtained from $\text{AlCl}_3/\text{DMSO}_2$ electrolytes by reduction of the solvated complex cation $[\text{Al}(\text{DMSO}_2)_3]^{3+}$. The reduction of $[\text{AlCl}_4]^-$ is not observed within the electrochemical window of these electrolytes. Aluminum electrodeposits formed by potentiostatic method from $\text{AlCl}_3/\text{DMSO}_2$ electrolytes exhibit fine grain size, relatively smooth surface and high purity (Legrand et al. 1995). Aluminium electrodeposition in $\text{AlCl}_3/\text{DMSO}_2$ electrolytes can be carried out for a long time, and a continuous running of this

process is feasible. Moreover, impure Al materials can be effectively purified via electrolysis in $\text{AlCl}_3/\text{DMSO}_2$ electrolytes (Jiang et al. 2007).

Molecular structure of DMSO_2 (melting point of 108.9 °C) was studied by X-ray (Pierce and Hayashi 1961, Sands 1964) and gas electron diffraction (Oberhammer et al. 1970, Hargittai and Hargittai 1974) methods as well as by means of quantum chemistry (Clark et al. 2008) in vacuum at DFT and MP2 levels of theory. Similar studies on $[\text{Al}(\text{DMSO}_2)_3]^{3+}$ are not known. We have found only single Raman spectral study of AlCl_3 -LiCl-dimethyl sulfone solid (300 K) and molten (400 K) mixtures (Hargittai and Hargittai 1974) indicating octahedral coordination of the central Al atom. The aim of our study is to find optimal $[\text{Al}(\text{DMSO}_2)_3]^{3+}$ and DMSO_2 structures in DMSO_2 solutions at room temperature and at 400 K by means of quantum chemistry.

Method

The geometries of $[\text{Al}(\text{DMSO}_2)_3]^{3+}$ complex cation and neutral DMSO_2 molecule in the lowest (singlet) spin states were optimized without any symmetry restrictions at DFT (B3LYP hybrid functional) (Becke 1993) and MP2 (Head-Gordon and Head-Gordon 1994) levels of theory using standard cc-pVDZ basis sets (Woon and Dunning 1993) from the GAUSSIAN03 library (Frisch et al. 2004). The stability of the obtained structures has been tested by vibrational analysis (no imaginary vibrations). The solvent effects of DMSO_2 has been approximated by the DMSO ones (due to their similar sizes and shapes as well as equal relative permittivities $\epsilon_r = 47$ (Clark et al. 2008)) using the Integral Equation Formalism Polarizable Con-

tinuum Model (IEFPCM) (Tomasi et al. 1994, Cancès et al. 1997, Mennucci and Tomasi 1997, Mennucci et al. 1997). Electronic structure parameters have been evaluated in terms of Natural Bond Orbital (NBO) analysis such as natural charges for atoms and overlap-weighted bond orders for bonds (Carpenter and Weinhold 1988, Reed et al. 1988). All calculations have been performed using the GAUSSIAN03 program package (Frisch et al. 2004). Relative abundances of individual model systems at room temperature and at 400K were evaluated using Boltzmann distributions and their free energy data.

Results and discussion

Free DMSO_2 molecule (Fig. 1) is of C_{2v} symmetry with nearly tetrahedral coordination of S atom. Its two O atoms may be used for the coordination to central metal atoms and so DMSO_2 may serve as a monodentate or bidentate ligand. It implies possible $[\text{Al}(\text{DMSO}_2)_3]^{3+}$ structures of four types:

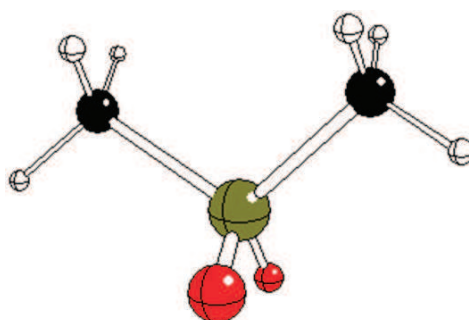


Fig. 1. MP2 optimized structure of DMSO_2 (O – red, S – yellow, C – black, H – white).

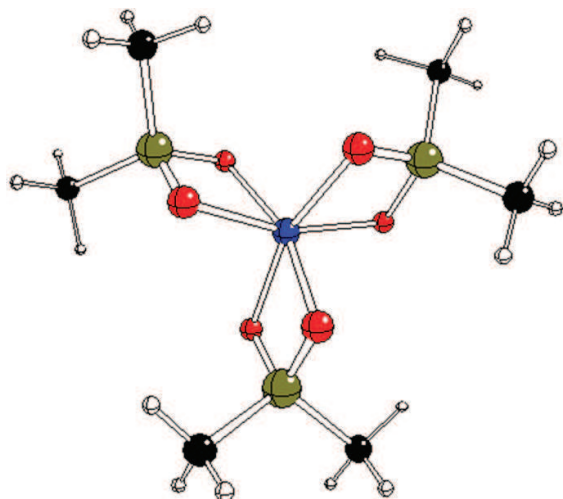


Fig. 2. MP2 optimized structure of $[\text{Al}(\text{DMSO}_2)_3]^{3+}$, model A (Al – blue, O – red, S – yellow, C – black, H – white).

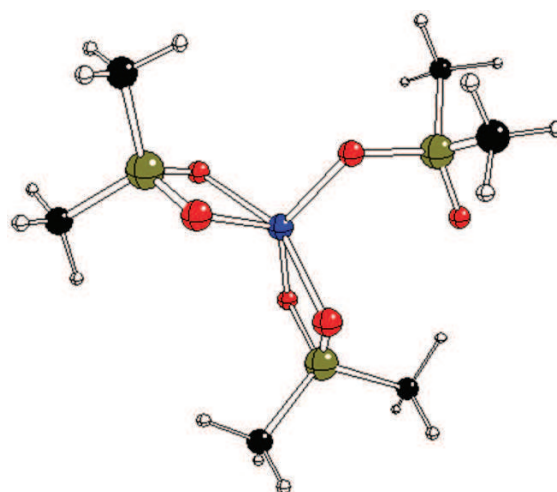


Fig. 3. MP2 optimized structure of $[\text{Al}(\text{DMSO}_2)_3]^{3+}$, model B (Al – blue, O – red, S – yellow, C – black, H – white).

- i) all three DMSO₂ ligands are bidentate (A model)
- ii) one monodentate and two bidentate DMSO₂ ligands (B model)
- iii) two monodentate and one bidentate DMSO₂ ligand (C models)
- iv) all three DMSO₂ ligands are monodentate (D models).

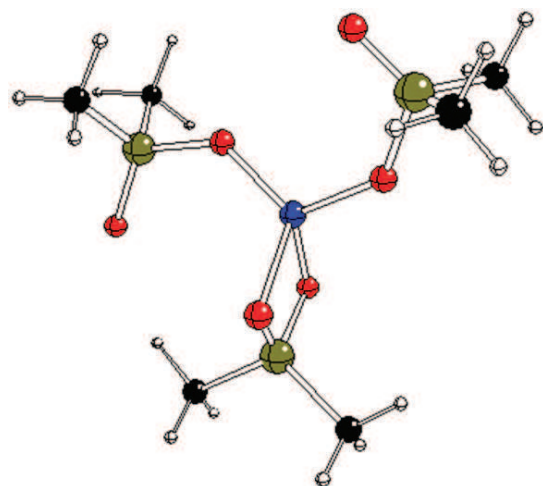


Fig. 4. MP2 optimized structure of $[\text{Al}(\text{DMSO}_2)_3]^{3+}$, model C1 (Al – blue, O – red, S – yellow, C – black, H – white).

The above mentioned $[\text{Al}(\text{DMSO}_2)_3]^{3+}$ model systems can be very simply distinguished according to Al-O distances (no bonding over 3 Å).

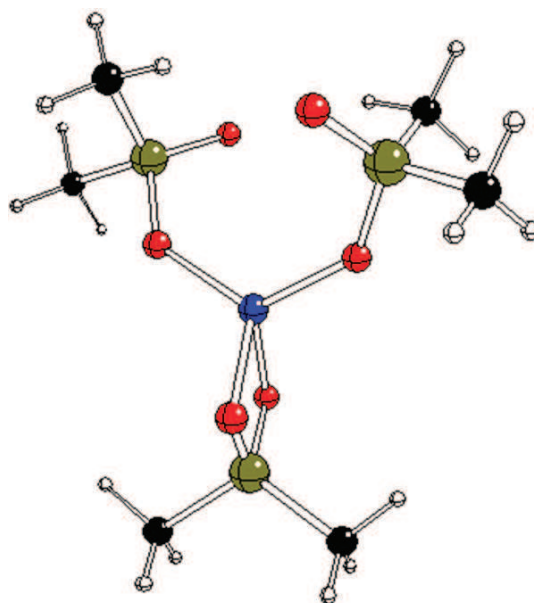


Fig. 5. MP2 optimized structure of $[\text{Al}(\text{DMSO}_2)_3]^{3+}$, model C2 (Al – blue, O – red, S – yellow, C – black, H – white).

Tab. 1. Optimized Al-O distances ($d_{\text{Al-O}}$), calculated absolute (G_T) and relative (ΔG_T) free energy data with relative occurrences of stable $[\text{Al}(\text{DMSO}_2)_3]^{3+}$ conformers at temperatures $T = 298$ K and 400 K.

Model	$d_{\text{Al-O}}$ [Å]	G_{298} [hartree]	ΔG_{298} [kJ/mol]	Occur. [%]	G_{400} [hartree]	ΔG_{400} [kJ/mol]	Occur. [%]
B3LYP method							
A	1.980 (6×) 1.985/1.929	-2127.12693	0.00	88	-2127.15260	0.00	62
B	1.928/1.981 3.469/1.791	-2127.12501	5.01	12	-2127.15200	1.59	38
C1	1.919/1.921 3.416/1.770 3.466/1.762	-2127.11511	31.03	0	-2127.14228	27.10	0
C2	1.918/1.915 1.770/3.442 3.293/1.773	-2127.11547	30.10	0	-2127.14275	25.85	0
MP2 method							
A	1.985 (6×) 1.993/1.940	-2123.09503	0.00	100	-2123.12083	0.00	99
B	1.939/1.989 3.384/1.794	-2123.08761	19.48	0	-2123.11436	17.24	1
C1	1.931/1.934 3.370/1.775 3.429/1.768	-2123.07464	55.53	0	-2123.10148	50.80	0
C2	1.929/1.927 1.776/3.378 3.216/1.783	-2123.07639	48.93	0	-2123.10332	45.98	0

Our results (Table 1) indicate the highest stability of the A model (Fig. 2) which dominates even at higher temperatures. It is of D_3 symmetry with two-fold axes in Al-S lines coincident with the twofold rotation axes of mutually turned DMSO₂ ligands. In agreement with the Raman study (Hargittai and Hargittai 1974), the central Al atom is hexacoordinated by six O atoms with nearly octahedral coordination. The B model (Fig. 3) is much less populated as indicated by MP2 data which are from the energetical point of view more reliable than the B3LYP ones. The population of both C models (Figs. 4–5), which differ in the mutual orientations of monodentate ligands, is vanishing. We have found no stable structures of D models type.

In the remaining part of our study of $[\text{Al}(\text{DMSO}_2)_3]^{3+}$ we will restrict to the A model only. Its S—O bond lengths are longer than in the free DMSO₂ ligand whereas the S—C ones exhibit reverse trends (Tab. 2). Lower O—S—O angles and the greater O—S—C and C—S—C ones than in the free ligand are caused by Al—O bonding in $[\text{Al}(\text{DMSO}_2)_3]^{3+}$. C—S—C (and

O—S—C) planes of individual ligands are turned by ca 60° as indicated by S^ˆ—Al—S—O dihedral angles (dashed atoms are related to the neighbouring DMSO₂ ligand). In free DMSO₂, the calculated S—O bonds are longer and O—S—O angles are greater than the experimental data. Except Al—O and C—H bonds, B3LYP bonds are longer than the MP2 ones. The differences between the angles obtained by these methods are vanishing.

As expected, only S and C atomic charges are negative (Tab. 3). More than one electron is transferred to Al central atoms from DMSO₂ ligands (ca 0.3–0.4 e per ligand). The comparison with free DMSO₂ (Tab. 3) implies that this charge difference is nearly equally distributed over all ligand atoms.

As expected, S—O bonds are the strongest ones both in the complex as well as in free DMSO₂ (Tab. 4). Al—O bonds are ca twice weaker than the remaining bonds. Weaker S—O and stronger S—C bonds in $[\text{Al}(\text{DMSO}_2)_3]^{3+}$ than in free DMSO₂ are implied by Al—O bonding. Only small differences between B3LYP and MP2 bond orders may be concluded.

Tab. 2. Structure data of $[\text{Al}(\text{DMSO}_2)_3]^{3+}$ – model A and DMSO₂ (dashed atoms are at the neighbouring DMSO₂ ligand).

System Method	$[\text{Al}(\text{DMSO}_2)_3]^{3+}$		DMSO ₂			
	B3LYP	MP2	B3LYP	MP2	Exp. ^{a)}	Exp. ^{b)}
Bond lengths [Å]						
O—S	1.552	1.545	1.495	1.486	1.431(4)	1.435(3)
S—C	1.782	1.761	1.806	1.785	1.777(6)	1.771(4)
C—H	1.099	1.100	1.097	1.099	?	1.114(3)
Bond angles [°]						
O—S—O	99.4	100.5	118.6	119.2	121.02(25)	119.7(11)
O—S—C	111.4	111.1	108.2	108.2	?	?
C—S—C	111.1	111.1	104.4	103.9	103.27(17)	102.6(9)
	105.5	105.7	105.5	105.7		
S—C—H	107.0	107.1	108.9	109.1	?	108.5(8)
	107.0	107.1	108.9	109.1		
Al—O—S	93.6	92.9	–	–	–	–
O—Al—O	73.4	73.6	–	–	–	–
O ^ˆ —Al—O	94.6/161.7/100.1	94.4/161.5/100.4	–	–	–	–
Dihedral angles [°]						
	-179.5	-180.2	-179.9	180.0		
C—S—C—H	59.9	60.4	61.1	61.2	?	?
	-60.1	-60.2	-61.0	-61.1		
S ^ˆ —Al—S—O	62.0	62.8	–	–	–	–
	-117.8	-117.5	–	–	–	–
S ^ˆ —Al—S—C	-27.6	-27.2	–	–	–	–
	152.4	152.8	–	–	–	–

Remarks:

^{a)} Pierce and Hayashi 1961.

^{b)} Hargittai and Hargittai 1974.

Tab. 3. Natural charges of individual atoms in $[\text{Al}(\text{DMSO}_2)_3]^{3+}$ – model A and DMSO_2 .

System Method	$[\text{Al}(\text{DMSO}_2)_3]^{3+}$		DMSO_2	
	B3LYP	MP2	B3LYP	MP2
Al	1.925	1.870	–	–
O	-0.959	-0.945	-0.964	-0.960
S	2.034	2.073	2.064	2.103
C	-0.809	-0.823	-0.855	-0.866
H	0.304	0.300	0.267	0.263
	0.313	0.310	0.260	0.256
	0.313	0.310	0.260	0.256

Tab. 4. Overlap-weighted NAO bond orders in $[\text{Al}(\text{DMSO}_2)_3]^{3+}$ – model A and DMSO_2 .

System Method	$[\text{Al}(\text{DMSO}_2)_3]^{3+}$		DMSO_2	
	B3LYP	MP2	B3LYP	MP2
O—S	0.841	0.842	0.994	0.998
S—C	0.801	0.801	0.751	0.750
C—H	0.749	0.742	0.754	0.746
	0.744	0.736	0.753	0.745
	0.744	0.736	0.753	0.745
Al—O	0.347	0.338	–	–

Finally it may be concluded that $[\text{Al}(\text{DMSO}_2)_3]^{3+}$ in molten DMSO_2 adopts the structure of the highest possible D_3 symmetry with bidentate DMSO_2 ligands in agreement with experimental data (Hargittai and Hargittai 1974). As indicated by relatively weak Al—O bonding, only ca one electron is transferred to Al from ligands and it implies only small structure and electron distribution differences between ligand and free DMSO_2 molecules. Further studies on $[\text{Al}(\text{DMSO}_2)_3]^{3+}$ discharging during aluminium electrodeposition are in progress.

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