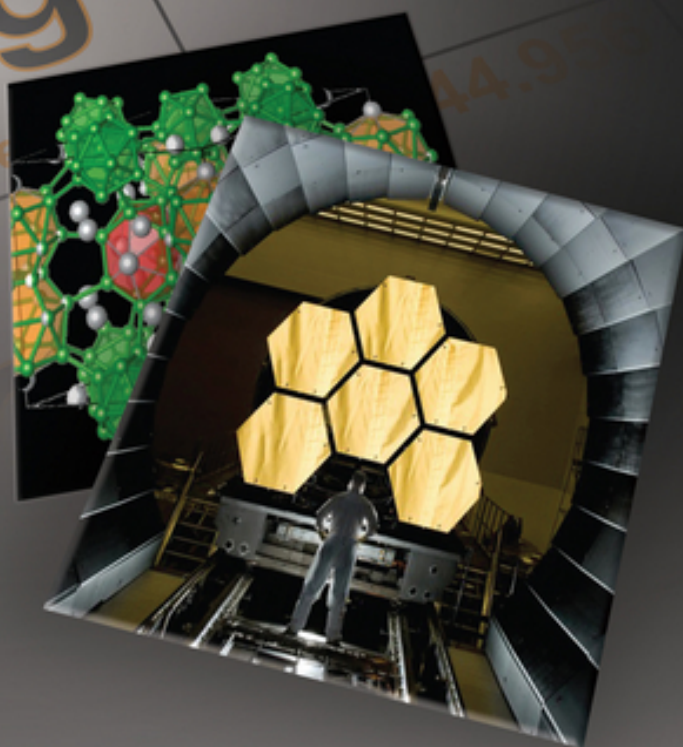


Editor
Timothy P. Hanusa

The Lightest Metals

Science and Technology
from Lithium to Calcium



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Figure 31 Frequency-stepped ^{27}Al CPMG NMR spectra of (a) AlMe_3 and (b) $\text{Al}(\text{NTMS}_2)_3$. The individual sub-spectra are shown on top with the corresponding total powder pattern shown on the bottom. Co-addition was used to form the total powder pattern. † and # indicate FM radio signal interference and impurities, respectively

Figure 32 Experimental (top) and simulated (bottom) static ^{27}Al powder patterns of $[\text{Cp}^*_2\text{Al}][\text{AlCl}_4]$ collected at 9.4 T. The patterns are dominated by the effects of the aluminum CSA

Figure 33 (a) ^{39}K NMR lineshapes for alkali metal C_{60} compounds, given in order of increasing lattice constant from top to bottom. ^{39}K NMR lineshapes at several temperatures for (b) K_3C_{60} , and (c) $\text{Rb}_2\text{KC}_{60}$

Figure 34 ^{39}K spin-echo MAS NMR spectra for the potassium aluminosilicates. All spectra were collected at 18.8 T using a spinning speed of ca. 15 kHz. The dashed line at 0 ppm is included for reference

Figure 35 Experimental ^{39}K MAS NMR spectra collected at 19.6 T. A spinning speed of 10 kHz was

used for G1 and G2 and a spinning speed of 8 kHz was used for G3, K(2'-AMP) and K(5'-ADP).

Figure 36 Experimental ^{39}K 1D MAS and 2D MQMAS NMR spectra of (a) KPic, (b) KGP, and (c) G4 collected at 19.6 T. The spinning speed was 8 kHz in all experiments and pure absorptive 2D spectra were collected by combing SPAM with the shifted-echo method. The t_1 increment in the MQMAS experiment was rotor synchronized. The sharp signal at 0 ppm in (a) results from trace amounts of micro domains within the solid

Figure 37 A comparison of (a) ^1H - ^{39}K BRAIN-CP/WURST-CPMG and (b) direct excitation ^{39}K DFS-QCPMG NMR spectra of potassocene (CpK) acquired at 9.4 T. The former took 128 scans and 10 min total acquisition time. The latter took 18 000 scans and 25 h total acquisition time (Schurko, 2015, unpublished data).

Figure 38 ^{25}Mg MAS NMR spectra of synthetic hydrotalcite acquired at 11.7 T. (a) unheated and heated to (b) 200 °C; (c) 300 °C; (d) 400 °C; (e) 600 °C; and (f) 1200 °C

Figure 39 Natural-abundance ^{25}Mg SPAM-3QMAS NMR spectrum of MgAl-25-NO_3^- . The dashed lines show the anisotropic slices of the three distinct Mg sites

Figure 40 Static ^{25}Mg SSNMR spectra of CPO-27-Mg as a function of rehydration degree. All spectra were acquired under identical experimental conditions. The * indicates a small amount of impurity likely resulting from magnesium oxide

Figure 41 7QMAS ^{43}Ca NMR spectrum of CaSiO_3 glass acquired at 21.8 T

Figure 42 (a) Simulated and (b) experimental ^{43}Ca MAS SSNMR spectra of CaCrO_4 collected with a spinning speed of 4 kHz. (c) Simulated and (d) experimental ^{43}Ca static SSNMR spectra of CaCrO_4 . Acquisition times of 18.9 and 5.2 h were required for (b) and (d), respectively, and all spectra were collected at 21.1 T

Figure 43 $^1\text{H}\{^{43}\text{Ca}\}$ R^3 -HMQC spectra of HA and tHA. A spinning speed of 8 kHz was used. The ^1H (black) and ^{43}Ca (red dashed) MAS NMR spectra are projected in the 2D spectra

Figure 44 ^9Be MAS NMR spectra of (a) Cp_2Be , (b) Cp^*_2Be , and (c) $(\text{C}_5\text{Me}_4\text{H})_2\text{Be}$ at 9.4 T, along with accompanying spectral simulations

Cation- π Interactions

Figure 1 Prototypical cation- π interactions of alkali metal cations with benzene. Optimized distances above the ring center and gas-phase interaction energies (E_{int} , in kcal mol^{-1}) are based on high-accuracy gas-phase computations from Sherrill and coworkers¹

Figure 2 Molecular electrostatic potential (MEP) plots of benzene, toluene, benzonitrile, and triazine. In these plots, the electrostatic potential is shown on an electron density isosurface ($\rho = 0.001 e \text{ bohr}^{-3}$)

Figure 3 DFT computed interaction energies, relative to the unsubstituted case ($\text{X} = \text{H}$), for model complexes of Na^+ above the center of monosubstituted benzenes, $\text{C}_6\text{H}_5\text{X}$, vs (a) the

electrostatic potential computed at the position of the Na^{\pm} above the ring and (b) the Hammett σ_m constant for the substituent

Figure 4 Competing models of substituent effects in cation- π interactions. (a) In conventional views, substituent effects arise from the modulation of the aromatic π -electron density by the substituents. (b) In the local dipole model of Wheeler and Houk,²⁹ substituent effects in cation- π interactions are dominated by the through-space electrostatic interaction of the local dipole associated with the substituent and the cation. Both models tend to provide similar predictions with regard to substituent effect trends

Figure 5 The electrostatic potential in the plane bisecting benzonitrile (left), as well as an additive approximation of this electrostatic potential constructed by adding the electrostatic potential in the plane bisecting benzene to the electrostatic potential of HCN

Figure 6 Accurate gas-phase interaction energy of Na^{\pm} with benzene (gray line) and benzonitrile (black line) as a function of distance above the ring. Also shown are a simple charge-dipole interaction (red line) and the result of adding this charge-dipole term to the Na^{\pm} ...benzene interaction potential (red dashed line).

Figure 7 Structure of the T1 lipase studied by Matsumura *et al.*,¹¹⁸ which exhibits a well-defined cation- π interaction between Na^{\pm} and a nearby Phe residue (PDB: 2DSN).

Ion Channels and Ionophores

Figure x.1 Natural transmembrane transport mechanisms: (from left) protein-based ion channel, barrel stave, helical peptide dimerization, and ionophore

Figure 2 Artificial transmembrane transport mechanisms: (from left) amphiphilic ion pair, channel-forming peptide, membrane-spanning molecule, barrel-hoop channel, and ionophore

Figure 3 Examples of polyether ionophores: (a) monensin, (b) nonactin, (c) salinomycin, (d) calcimycin, (e) ionomycin, (f) nigericin, and (g) lasalocid

Figure 4 X-ray structures of polyether ionophore cation complexes with solvent molecules removed for clarity: (a) (Li·monensin) (CSD ID: DOPVEJ), (b) (Na·monensin) (CSD ID: BELDAX), (c) (K·monensin) (CSD ID: FECROU10), (d) (Na·nonactin) (CSD ID: NONACS), (e) (K·nonactin) (CSD ID: NONKCS), (f) (Ca·nonactin) (CSD ID: CAXHEO), (g) (Na·salinomycin) (CSD ID: GIZDIC), (h) (Mg·(calcimycin)₂) (CSD ID: DUJWOU), (i) (Ca·ionomycin) (CSD ID: IONCAH01), (j) (Na·nigericin) (CSD ID: NIGERI), (k) (Na·lasalocid) (CSD ID: NALASC), (l) (Ba·(lasalocid)₂) (CSD ID: KAFZIA); CSD, Cambridge Structural Database

Figure 5 Cyclopeptide ionophores: (a) valinomycin, (b) enniatin A, and (c) beauvericin

Figure 6 X-ray structures of cyclopeptide ionophore cation complexes with counterions removed for clarity: (a) [K·valinomycin][±] (CSD ID: TEFBAH), (b) [K·(enniatin B)₂][±] (CSD ID: PEKFEQ), and (c) [(Ba·beauvericin)₂]⁴⁺ (CSD ID: BEAVBA); CSD, Cambridge Structural Database

[Figure 7 Examples of artificial ionophores](#)

[Figure 8 Top and side views of natural transmembrane channel-forming proteins \(not to scale\): \(a\) ASIC \(PDB ID: 2QTS\), \(b\) KcsA \(PDB ID: 1BL8\), \(c\) CavAb \(PDB ID: 4MS2\) \(d\) NavAb \(PDB ID: 3RVY\), and \(e\) TmCorA \(PDB ID: 4EED\); PDB = Brookhaven Protein Data Bank](#)

[Figure 9 Examples of channel-forming biomolecules: \(from top\) amphotericin, nystatin, alamethicin, and magainin](#)

[Figure 10 Peptide-based artificial transmembrane channel-forming molecules](#)

[Figure 11 Examples of nonpeptide-based artificial channel-forming molecules](#)

Aryllithiums and Hetarylithiums: Generation and Reactivity

[Figure 1 *n*-BuLi/anisole complexation illustrating electron withdrawal](#)

[Figure 2 Early transition state depiction for ortho-metalation of anisole \(metal, M = Li\)²⁵](#)

[Figure 3 Ether \(e\)-stabilized structures of *n*-BuLi, for the tetramer \(**1**\), for the dimer \(**2**\), and for the bis-chelating amine-stabilized structure of the dimer \(**3**\).](#)

[Figure 4 Bis-chelating amines used to accelerate metalation reactions: diazobicyclo\[2,2,2\]octane \(DABCO\), tetramethylethylenediamine \(TMEDA\), pentamethyldiethylenetriamine \(PMDTA\), and hexamethylphosphorotriamide \(HMPTA\)](#)

[Figure 5 Proposed intermediate for ortho-lithiation⁶⁴](#)

[Figure 6 The “pair of tweezers” representation for the cooperative 2-metalation of 1,3-DMB⁸⁵](#)

[Figure 7 Preferred sites of lithiation of five-membered ring heterocycles \(h are the heteroatoms O, S, or NMe\)](#)

[Figure 8 Nearly linear structure for the X/Li intermediate](#)

Magnesium and Calcium Complexes in Homogeneous Catalysis

[Figure 1 Increasing popularity of molecular alkaline earth catalysis. \(a\) Number of publications per year; \(b\) Number of citations per year](#)

[Scheme 1 General stoichiometric reactivity of alkaline earth complexes](#)

[Figure 2 Standard catalytic cycles observed in Group 2-mediated reactions](#)

[Scheme 2 Homoleptic and heteroleptic benzylcalcium precatalysts for styrene polymerization](#)

[Scheme 3 Dissociative mechanism of carbanionic polymer chain end inversion during calcium-catalyzed styrene polymerization](#)

[Figure 3 Possible microstructure outcomes for lactide ROP](#)

[Scheme 4 Mechanisms of lactide ROP](#)

[Figure 4 Selection of highly efficient heteroleptic magnesium and calcium precatalysts for lactide ROP](#)

[Scheme 5 Influence of chelate-resting state on catalytic activity toward LA and \$\epsilon\$ -CL](#)

[Figure 5 Tischenko reaction with homoleptic and heteroleptic Group 2 amides and proposed mechanism](#)