Charge Density Analyses in Polyimido Sulfur Ligands Yield Single Molecule Magnets

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Sulfur was long believed to underdo valence expansion,[1] not obeying the eight-electron rule.[2] In a charge density investigation of sulfate we could disprove this theorem.[3] The same is valid for polyimido sulfur compounds $S(NR)_n^{m-}$ with n=2-4; m=1,2.[4] In the tetraimido sulfuric acid $H_2S(NtBu)_4$ we showed recently that most in the formal S=N*t*Bu and S-N(H)*t*Bu is electrostatics on top of covalent σ-bonding but virtually no π-bonding.[5] This lack of orbital control is beneficial for single-molecule magnets, because the N-[M]-N angle can ideally be adapt to the metal's requirements to increase magnetic anisotropy.[6] This way we could optimize d- and f-metal SMMs.[7]

{1} Pauling, L. The nature of the chemical bond; Cornell University Press, Ithaca, NY, ***1939****.*
{2} Lewis, G. N. J. Am. Chem. Soc. ***1916****, 38, 762-785.*
{3} Gatti, C.; Stalke, D.; Iversen, B. B.; et al. Inorg. Chem. ***2012****, 51, 8607-8616.*
{4} Stalke, D.; et al. J. Am. Chem. Soc. ***2004****, 126, 1781.*
{5} Stalke, D.; et al. Angew. Chem. Int. Ed. ***2021****, 60, 5679-5682.*
{6} Overgaard, J.; Stalke, D.; et al. Eur. J. Inorg. Chem. ***2021****, 3108-3114.*
{7} Stalke, D.; et al. Inorg. Chem. ***2021****, 60, 13982-13989.*

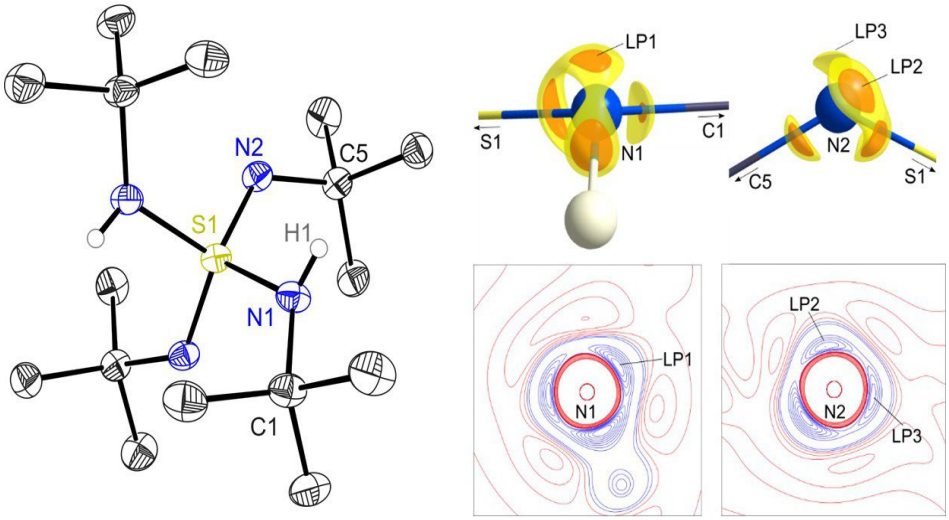

Figure 1