

A NEW SET OF MOLECULAR DESCRIPTORS

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A new set of criteria for quantitative analysis of molecular interactions is proposed resulted from the investigation of crystal structures of 808 pi-complexes of rare-earth atoms (Ln). The set is based on the conceptions of atomic and molecular Voronoi-Dirichlet polyhedra and comprises: I. The criteria of existence of agostic and van der Waals contacts Ln...H-L between the complexing atom Ln and a ligand L. II. A set of criteria for ligands, namely: ligand total, valent and agostic solid angles, which are to be calculated with the faces of Voronoi-Dirichlet polyhedron of the Ln atom corresponding to all, only valent or only agostic Ln-L contacts, respectively; and ligand residual solid angle which is the difference between total and valent solid angles. III. A set of criteria for complexes as a whole including similar terms as the previous set, but relating to entire complex particle, to be calculated by summation of corresponding ligand solid angles for all ligands in a given complex. It is shown that the criteria of the first set allow one to improve the conclusions about existence or missing of agostic contacts. Seven different numerical combinations of the second and third sets of criteria were singled out, with which one can predict the composition and sterical stability of complex groups, the existence of intra- and intermolecular agostic and van der Waals interactions, and can judge about the capability of a ligand L to screen the central atom and to form the agostic contacts Ln...H-L.

Keywords: AGOSTIC INTERACTIONS, π -COMPLEXES

THE CRYSTAL AND MOLECULAR STRUCTURE OF (BIS N-OCTYL-HYDROXYNAPHTHALDIMITATOCOPPER(II))

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N-alkyl substituted Schiff bases with aliphatic long chains has been used to synthesize a variety of coordination compounds. Liquid crystals properties and Langmuir-Boldgett films has been intensively studied during the last years for these kind of materials (1). The present study show the synthesis, conventional characterization and X-ray structure for bis N-octyl-hydroxynaphthaldimitatocopper(II) complex. It crystallizes in the R-3 space group with $a = b = 42.260(25)$ Å, $c = 5.162(3)$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$, $Z = 9$, $V = 7984(14)$ Å³. A total of 1389 reflections with F greater than four times $\sigma(F)$ were refined to a value of $R = 0.0664$. The molecular structure shows the copper atom in a planar environment and the octyl chains parallel each other. The crystal packing shows stacked units intermolecularly separated by 3.61 Å, probably due to pi-pi electron interactions between naphthyl groups.

References

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COMPLEX COINAGE METAL (I) THIOSULFATES

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Crystals formed from aqueous solutions of thiosulfates (i.e. Na, K, and NH₄) and coinage metal halides, may be relevant photographic 'fixation'. Previously known members of the isomorphous, tetragonal $I-42d$ $M^1_9M^2X_2(S_2O_3)_2$, $M^1 =$ group 1 cation $M^2 =$ (Cu, Ag), series, including new members, have been isolated as eight complexes, the nitrates and the potassium adduct all new, containing the complex anion $[M^2(SSO_3)_4]^{7-}$ with quasi tetrahedral S-M-S geometry. Salts of the form $M^1_{2n-1}M^2(S_2O_3)_n \cdot xH_2O$, $n = 1-3$, have also been defined: For $n = 3$, $M^2 =$ Cu, $M^1/x = K/2.25$ or $1/5/6$, NH₄/6, (and also for the (NH₄)₄Na/4H₂O.MeOH adduct) the arrays take the form $M^1_5[Cu(SSO_3)_3] \cdot xS$ with distorted trigonal planar CuS₃ coordination environments; the silver counterparts take the form $M^1_{10}[(O_3SS)_2Ag(\mu-SSO_3)_2Ag(SSO_3)_2]$ for $M^1 =$ K, NH₄. For $n = 2$ adducts have only been defined for $M^2 =$ Ag, the anions of the $M =$ Na, K adducts being dimeric and polymeric: $Na_6[(O_3SS)_2Ag(\mu-SSO_3)_2Ag(SSO_3)_3] \cdot 3H_2O$, $K_3[Ag(\mu-SSO_3)_2] \cdot H_2O$; a polymeric copper 1 counterpart of the latter is found in $Na_5Cu(NO_3)_2(S_2O_3)_2 = 2NaNO_3 \cdot Na_3[Cu(\mu-SSO_3)_2]$. For $n = 1$, NaAgS₂O₃, isolated as both the known mono- and a new anhydrate, exhibit a two-dimensional polymeric complex anion in both forms but with different contributing motifs, 6 and 4 membered rings respectively. (NH₄)₁₃Ag₅(S₂O₃)₈ · 2H₂O takes the form (NH₄)₁₃{[OSS]₃Ag(μ-SSO₃)₂Ag], a linear central silver atom linking a pair of [Ag(SSO₃)₃]⁷⁻ entities. In Na₆[(O₃SS)Ag(μ-SSO₃)₂Ag(SSO₃)₃] · 3H₂O, two binuclear anions are present as single clusters, the associated oxygen atoms disposed to one side, sandwiching layers of sodium ions.

Keywords: COINAGE METAL THIOSULFATE CRYSTAL STRUCTURE

EPR EVIDENCE FOR AN INTRAMOLECULAR C-F...V INTERACTION IN VANADA(IV)AZIRINE COMPLEXES BASED FROM X-RAY STRUCTURE DETERMINATIONS

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The vanadocene Cp₂V is a valuable reactive complex able to react with alkynyl unit. The formation of a vanadocyclopropene moiety was already demonstrated when Cp₂V is reacted with an alkyne. New situation bonding can be reached with rich acetylenic chemistry in which the synthon Cp₂V play an important part in this concept. Extension of this research to the reactivity of the nitrile - CN triple bond towards Cp₂V was recently achieved. Reaction of vanadocene Cp₂V with 'activated' nitrile R1CN.L (L: Lewis acid) yields the borane adduct of vanada(IV)azirine complexes Cp₂V(eta:2-R1C = N.L) (L = B(C₆F₅)₃ and B(2,6-F₂C₆H₃)₃). According to their structures, the Cp₂V vanadocene moiety is bonded to the nitrogen and carbon atoms of the ligand framework, to form the vanadaazirine ring. EPR studies in fluid solution were conducted on these complexes. A doublet of octets due to the coupling of the unpaired electron of the vanadium with the 51V (I = 7/2) nucleus and to an additional hyperfine coupling to a ortho-F atom bared by the phenyl ring of the borane is elucidated by means of the different Lewis acid used in this work. A contrario, expected 8 line pattern EPR is observed with L = B(3,4,5-F₃C₆H₂)₃, in which no ortho-F is present in the phenyl ring. This different EPR behavior gives evidence for the presence of a C-F...V interaction in fluid solution with L = B(C₆F₅)₃ and B(2,6-F₂C₆H₃)₃. A dynamic process along the rotation of B-C and N-B allows the ortho-fluorine atom to approach the vanadium centre. A model can be drawn to take into account this flexibility and V...F distances between V and ortho-F atoms are in the expected range for such an interaction.

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