Dynamics of Ligands and Water Molecules in Trinuclear Carboxylate Complexes

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Trinuclear transition metal complexes of the general formula $[M_3O(L)_6(L_t)_3]$ (M = transition metal, L = bidentate bridging ligand, L_t = terminal ligand) with central oxygen atoms have proven to be important model compounds for studying basic chemical and physical phenomena.[1] In order to study the dynamics of ligands and water molecules in such trinuclear carboxylate complexes, Stride et al.[2] performed incoherent inelastic neutron scattering (IINS) experiments on the chromium acetate complex $[Cr_3O(CH_3CO_2)_6(H_2O)_3]Cl \cdot 5\,H_2O$ (CRAC, CRACHH) as well as on partially deuterated ($[Cr_3O(CH_3CO_2)_6(D_2O)_3]Cl \cdot 5\,D_2O$ (CRACHD), $[Cr_3O(CD_3CO_2)_6(H_2O)_3]Cl \cdot 5\,H_2O$ (CRACDH)) and isotopically diluted species (about 5% H; $[Cr_3O(CD_3CO_2)_6(D_2O)_3]Cl \cdot 5\,D_2O$ (CRACDD)). Because of the large scattering cross-section of hydrogen atoms the observed IINS signals were assigned to vibrations of the acetate methyl groups and especially to the vibrations of the ligands and hydrate H_2O molecules, that is, the bending mode (δ(HOH)), the rocking ($\rho(H_2O)$ or $r(H_2O)$), wagging ($\omega(H_2O)$ or $\gamma(H_2O)$), and twisting libration ($\tau(H_2O)$ or $t(H_2O)$) as well as the $Cr{-}OH_2$ translational mode ($\nu(CrOH_2)$).[3]

In the case of HDO molecules, which are present in partially deuterated and isotopically diluted species (in addition to H_2O and D_2O molecules), intramolecular coupling of the OH and OD stretching vibrations as in the case of H_2O and D_2O is no longer possible. This is claimed correctly by Stride et al.[2] The frequency of the observed OH stretching vibration of HDO then resembles the mean value of the frequencies of the symmetric (ν_{sym}) and the antisymmetric OH stretching mode (ν_{asym}) of the H_2O molecule. Analogous considerations can be made for out-of-plane librations ($\gamma(H_2O)$ and $t(H_2O)$),[4, 5] as was likewise undertaken by Stride et al.[2] In the case of the in-plane vibrations (δ(HOH) and $r(H_2O)$), however, this is not possible. Since δ(HOH) is an internal mode, predominantly covalent bonds within the H_2O, HDO, and D_2O molecules are strained. The rocking vibration ($r(H_2O)$), however, is an external vibration, and the molecules vibrate more or less as rigid units. The rocking vibration is primarily controlled by lattice forces. The assumption discussed by Stride et al.—namely, that the frequency of the in-plane OH and the OD bending vibrations of HDO molecules resembles the mean value of the frequencies of δ(HOH) and $r(H_2O)$ or δ(DOD) and $r(D_2O)$[2]—is completely unfounded. Therefore, the bending mode of HDO molecules (δ(HDO)) in solid hydrates and aqua complexes is observed in the range from 1400 to 1460 cm^{-1},[5] and not at about 970 cm^{-1} as assumed by the authors. At least in this respect, the paper by Stride et al.[2] has to be corrected.

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[1] R. D. Cannon, R. P. White, *Prog. Inorg. Chem.* **1988**, *36*, 195.

[2] J. A. Stride, U. A. Jayasooriya, J. Eckert, *Angew. Chem.* **1999**, *111*, 172; *Angew. Chem. Int. Ed.* **1999**, *111*, 116.

[3] In the case of the librational modes, the symbols used in the cited paper (ref. [2]) are opposed to the commonly used ones.

[4] A. Eriksson, J. Lindgren, *Acta Chem. Scand. A* **1978**, *32*, 737.

[5] H. D. Lutz, *Struct. Bonding (Berlin)* **1988**, *69*, 97.

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