

TEMPERATURE DEPENDENT BOND DISTANCE VARIATION IN Ni COMPLEXES WITH SOME POLYAMINE LIGANDS

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X-ray structure determinations of $[\text{NiCl}(\text{H}_2\text{O})(232\text{-tet})]\text{Cl}$ (1) and $[\text{Ni}(\text{H}_2\text{O})_2(323\text{-tet})]\text{Cl}_{2.32}\text{H}_2\text{O}$ (2) were carried out at the temperature between 123 to 293K (232-tet = N,N-f-bis(2-aminoethyl)-1,3-propanediamine; 323-tet = N,N-f-bis(3-aminopropyl)ethylene-diamine). The polyamine ligands are both coordinated in planar conformation, and the bond lengths of Ni to axial ligands are largely affected by the temperature. For 1, Ni-Cl and Ni-O distances of 2.475 and 2.176 Å respectively at 130 K is elongated to 2.485 and 2.192 Å respectively at 293 K, while the averaged Ni-N length are 2.082 and 2.083 Å for 130 and 293 K, respectively. Those for 2 are 2.142 to 2.165 Å for averaged Ni-O distances and 2.100 to 2.098 Å for the averaged Ni-N length, respectively.

Keywords: NICKEL COMPOUNDS TEMPERATURE DEPENDENT BOND DISTANCE POLYAMINE COMPLEX

STRUCTURE DETERMINATIONS OF POLYOXOTUNGSTATES USING HIGH-ENERGY SYNCHROTRON X-RAY DIFFRACTION

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One of the most serious problems encountered during the structure determinations of polynuclear inorganic/organometallic compounds containing heavy elements comes from the systematic error of the measured diffraction intensities caused by the effect of absorption. The best way to avoid this problem is, of course, to carry out perfect absorption corrections, which are in many cases not achievable. As a more practical and essential clue to this problem, we have installed an image-plate Weissenberg camera with an integrated automated image-plate reader into the BL04B2 beamline of SPring-8¹. Since this beamline utilizes monochromatic X-rays with the energy higher than 37.78 KeV, attenuation coefficients of many heavy elements are dramatically reduced from those for MoK_α radiation, in a typical case, by a factor of a seventh. Results obtained here include a structure analysis of a tetrabutylammonium β -dodecatungstosilicate, $[(\text{C}_4\text{H}_9)_4\text{N}]_4[\text{SiW}_{12}\text{O}_{40}]\cdot\text{H}_2\text{O}$, which was carried out WITHOUT any absorption corrections. The ADP's both for W and O atoms show very small anisotropy. The standard uncertainties associated with the interatomic distances obtained from this structure analysis are as low as 0.005 Å for W-O distances and 0.0005 Å for W-W distances. The positional parameters that were precisely refined allowed us detailed interpretations of the structural parameters, thus leading to the first observation of a distortion of the β -Keggin W_{12} framework from the ideal C_{3v} symmetry down to the C_3 symmetry.

References

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Keywords: SYNCHROTRON RADIATION POLYOXOMETAL ATE HIGH-ENERGY X-RAY

CRYSTALLOGRAPHIC STUDY OF ANHYDROUS HYPOPHOSPHOROUS ACID SALTS $\text{M}(\text{H}_2\text{PO}_2)_2$

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Anhydrous metal hypophosphites find various practical applications and have been used for studies of various aspects of solid-state reactivity. At the same time, their crystal structures are not adequately known and analyzed. The present contribution is aimed to review the structural data on metal hypophosphite from a unifying point of view. The crystal structures of anhydrous Be, Ca, Ba, Cu, and Cd have been determined by X-ray single crystal analysis during this study. The crystal structure of anhydrous Zn hypophosphite is known. Using powder diffraction method that Sr, Ba and Pb hypophosphites are isostructural were shown. The geometry of the hypophosphite anion in the reviewed crystal structure is very close to the idealized one, with point symmetry $mm2$ with O-P-O and H-P-H angles are about 115 and 100 degrees respectively. Hypophosphite anions and metal cations have tendency to form polymeric sandwich layers. The metal cations surrounded by hypophosphite anions from both sides and lie inside layer. The surface of layer consist of hydrogen atoms from hypophosphite anions. The structure of layer is close to one of the CdI_2 structure. In spite of differences in coordination of metal cations by hypophosphite anions the whole organization of layer remain the same. The differences consist in stacking of hypophosphite anions relatively metal cations network. Separate layers in all compounds are linked to each other by van der Waals interactions.

Keywords: STRUCTURE, HYPOPHOSPHITE, ISOMORPHISM

LINEAR PENTANUCLEAR METAL STRING COMPLEXES: SYNTHESIS, STRUCTURES, AND REDOX PROPERTIES

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Much attention has been paid to linear multinuclear metal string complexes due to their attractive properties such as strong metal-metal interactions in the molecules and their potential for the applications as molecular electronics. A series of pentanuclear metal string complexes $[\text{M}_5(\text{tpda})_4\text{LL}']$ ($\text{M} = \text{Ni}(\text{II}), \text{Co}(\text{II}), \text{Cr}(\text{II})$; $\text{tpda} = \text{tripyridyldiamido dianion}$; $\text{L}, \text{L}' = \text{axial ligands}$) have been synthesized and their redox reactivities have been studied. In the nickel complexes, the neutral complex $[\text{Ni}_5(\text{tpda})_4\text{Cl}_2]$ has a symmetrical structure with no metal-metal bonding. The one-electron oxidized complex $[\text{Ni}_5(\text{tpda})_4(\text{CF}_3\text{SO}_3)_2]^+$ adopts an unsymmetrical structure and exhibits metal-metal interactions. In the cobalt complexes, the neutral complex $[\text{Co}_5(\text{tpda})_4\text{Cl}_2]$ also has a symmetrical structure with bond order of 0.5 in each Co-Co bond. The one-electron oxidized complex $[\text{Co}_5(\text{tpda})_4\text{Cl}_2]^+$ has almost identical structure and bonding feature. In the chromium series, the neutral complex $[\text{Cr}_5(\text{tpda})_4\text{Cl}_2]$ also has a symmetrical structure with bond order of 1.5 in each Cr-Cr bond. Both one- and two-electron oxidation products adopt an unsymmetrical structure, in which the Cr_5 core has the alternation of quadruple bonds and no bonds. The differences in the metal-metal interactions between the neutral and oxidized complexes might shed light on the application of these metal string complexes as 'molecular switches'.

Keywords: METAL STRING COMPLEX MOLECULAR METAL WIRE MOLECULAR SWITCH