range with a lifetime of 20 ms at 77 K.[10]

Discussion

Luminescence Band Energies and Assignments. The luminescence spectra of the cubic tetrameric silver compounds $[AgP(OCH_3)_3Cl]_4$ and $[AgPPh_3Cl]_4$ were recently reported.[1] The emission band maxima were at 20 800 cm^{-1}. These bands were assigned to a transition in the cubic $[AgCl]_4$ moiety from the bonding combination of silver 5s orbitals to an antibonding combination of silver 4d orbitals.[1] The energy of the 5s–4d transition is 39 164 cm^{-1} in the free Ag^+ ion[11] and about 40 000 cm^{-1} in silver ions doped in NaCl.[12] The very large red shift from the isolated silver ion to the silver clusters was attributed to significant interactions between the silvers in the latter compounds.[1]

The assignment of the emission to transitions between interacting s and d orbitals on adjacent silver ions is supported by direct spectroscopic evidence for interactions between other d^{10} M^+ ions in dimeric compounds,[13] those doped in salts,[14] and those doped in other inorganic hosts.[15] The emission from Pd_2(bis(diphenylphospino)methane)$_3$ was assigned to a metal–metal $\sigma^* \rightarrow \sigma$ transition. Excited-state Raman spectroscopy showed that the Pd–Pd bonding is strengthened in the excited electronic state.[16] In $SrCl_2$, Cu^+ monomers emit with a band maximum at 22 200 cm^{-1} and Cu_2^{2+} dimers emit with their maximum at 17 000 cm^{-1}. In β''-alumina, copper monomers emit at about 24 000 cm^{-1} and the dimers at about 19 000 cm^{-1}.[15] The copper ions are mobile in the conduction plane of β''-alumina, and the photoexcitation of one ion causes formation of a Cu_2^{2+} excimer that emits at much lower energy than the monomer. Photoexcitation of β''-alumina doped with both Ag^+ and Cu^+ causes formation of a $AgCu^{2+}$ exciplex that emits at much lower energy than either of the monomers.[17] In all of these cases, the emission is assigned to a transition from the metal–metal bonding orbital formed by interaction between the s orbitals to a metal–metal antibonding orbital formed from the interaction between the d orbitals. In the β''-alumina matrix, the excited state is metal–metal bonding and the mobile ions form dimers. This bonding interaction is likely to cause shortening of the distances between the silver ions in the excited state of the tetrameric clusters.

The silver–silver interaction model provides a simple explanation for the energy differences between the emission band maxima of the cube and chair isomers. In the cube isomer (structure I), each of the four silver atoms has three neighboring silver atoms. In the chair isomer (structure II), only two of the silvers have three neighboring silver atoms whereas the other two silvers have only two silver neighbors. This simple correlation suggests that the LUMO–HOMO transition is at lower energy in the cube because the delocalization over the d and s orbitals of the silver atoms in the cube is larger than that in the chair. The silver–silver distances in the ground electronic state cannot be used to explain the relative transition energies. The silver–silver interaction model would predict that the shortest distance would result in the lowest transition energy, but the shortest distance is 3.09 Å in the chair and 3.12 Å in the cube. The interactions between the silver atoms in the excited state play the dominant role.

Lifetimes of the Luminescences. Luminescence lifetimes of the order of microseconds are typical of "spin-forbidden" transitions in metal complexes where the large spin–orbit coupling makes the transitions partially allowed. The lifetime of the chair isomer is significantly longer than that of the cube. (No lifetime data were reported for the silver clusters containing the chloro ligand.) Simple explanations for these lifetimes within the framework of the silver–silver interaction model are provided by the number of heavy atoms and the number of ligands with high-frequency vibrations that are involved. In the cube isomer, the emitting state could involve the orbitals on all four silver atoms as well as those on the four iodide ligands and the four phosphine ligands. In the chair isomer, the emitting state could involve the orbitals on at most three silver atoms, three iodide ligands, and three phosphine ligands. The large number of heavy atoms involved in the cube isomer's orbitals could shorten the lifetime because of an increased radiative rate constant caused by the large spin–orbit coupling. The larger number of triphenylphosphine ligands involved in the cube isomer's orbitals could also shorten the lifetime because of an increased nonradiative rate constant caused by the larger number of high-frequency ligand vibrations.

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Registry No. $Ag_4I_4(PPh_3)_4$ (cube isomer), 54937-07-4; $Ag_4I_4(PPh_3)_4$ (chair isomer), 54999-20-1.

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Additions and Corrections

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Jean-Marc Giraudon, Jean Sala-Pala,* Jacques E. Guerchais,* Yves Le Mest, and Loïc Toupet: Interconversion of Mononuclear and Quadruply Bonded Dinuclear Dibenzotetraaza[14]annulene Complexes of Molybdenum.

Page 891. The fourth author's name was omitted from the original byline.—Jean Sala-Pala and Jacques E. Guerchais

Martin W. Payne, Peter K. Dorhout, and John D. Corbett*: Heterometallic Condensed Cluster Compounds: Pr_4I_5Z (Z = Co, Ru, Os) and La_4I_5Ru. Synthesis, Structure, and Bonding.

Page 1470. In the first complete paragraph, third sentence, the correct magnetic moment per metal atom in Pr_4I_5Ru is $7.1 \times 4^{-1/2} = 3.6\ \mu_B$, substantially the classical value for Pr^{3+}. No unusual coupling is indicated.—John D. Corbett