Conclusion

Enhanced paramagnetic contributions due to decreasing ΔE(HOMO–LUMO) and due to a larger antipodal B_{2p} character of the HOMO may qualitatively rationalize the computed trends in $\delta(^{11}B)$ of the antipodal boron B(10). Since the computed ΔE values do not parallel the IGLO chemical shifts of B(10), the "polarization" of the HOMO seems to be the more important factor governing the A-effect in the 10-vertex series. In contrast to FCF, we predict heterofragments of less or similar electronegativity than the borane fragment (i.e. X = SiH^- or X = PH) to cause a substantial downfield shift of the antipodal boron. In this context, it is interesting to note that the A-effect in B_9H_9Se ($\delta(^{11}B)$ of B(10) 73.3 ppm[26]) is very pronounced.

The remaining question is, why is the antipodal effect in the 10-vertex cages so large? Further studies including 12-vertex heteroboranes that might provide insights in this problem are in progress.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Stiftung Volkswagenwerk. We thank Professor W. Kutzelnigg and Dr. M. Schindler for the Convex version of the IGLO program (which is available for distribution) and U. Fleischer for extensive discussion and advice. M.B. acknowledges a grant of the Studienstiftung des Deutschen Volkes. The calculations were performed on a Cray Y-MP4 computer of the Leibniz Rechenzentrum Munich and on a Convex C-210s computer of the Institut für Organische Chemie.

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(26) Friesen, G. D.; Kump, R. L.; Todd, L. J. *Inorg. Chem.* **1980**, *19*, 1485.

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Luminescence from the Chair and Cube Isomers of $Ag_4I_4(PPh_3)_4$

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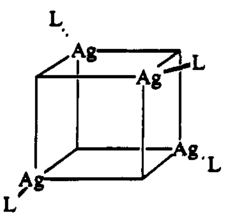
The luminescence properties of tetrameric metal clusters of the type $M_4X_4L_4$ where M is a d^{10} ion such as Cu^+, Ag^+, or Au^+, X = Cl^-, Br^-, or I^-, and L is a substituted pyridine or substituted phosphine are attracting increasing attention. Reports of the luminescence of clusters containing four Ag^+ ions,[1] four Au^+ ions,[2] four Cu^+ atoms,[3-6] and mixed Cu^+/first-row transition-metal ions[7] have recently appeared.

The tetrameric clusters generally exist in either a distorted cubane geometry, consisting of a M_4X_4 core, or a distorted chair structure. Idealized forms of these structures are sketched in I and II. The steric and electronic factors that lead to these geometries have been evaluated.[8] The compound $Ag_4I_4(PPh_3)_4$ is unusual because it undergoes a cube → chair isomerization and because the two geometric forms can be isolated by crystallization from different solvents.[8] It thus offers the unique opportunity to study the luminescence properties of the two isomers of the same tetrameric molecule. We report in this paper the luminescence spectra, temperature dependence, and lifetimes of the emission of the cube and chair forms of $Ag_4I_4(PPh_3)_4$.



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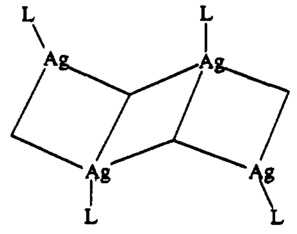

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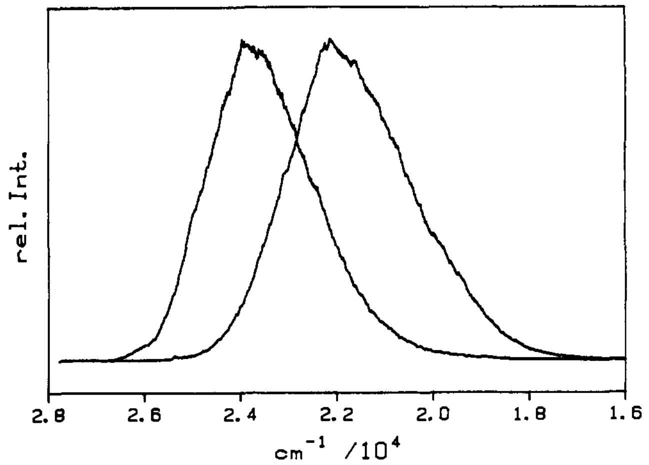

Figure 1. Luminescence spectra of solid samples of the chair (left) and the cube (right) forms of $Ag_4I_4(PPh_3)_4$ at 12 K.

Experimental Section

The tetrameric $Ag_4I_4(PPh_3)_4$ compound was prepared according to the literature procedure.[8] The cube isomer was prepared by crystallization from $CHCl_3/Et_2O$, and the chair isomer, by crystallization from CH_2Cl_2/Et_2O.

Emission spectra were obtained from microcrystalline samples of the compounds at temperatures between 12 and 120 K by exciting them with the 351- and 363-nm lines from an argon ion laser. The samples were mounted on an OFHC copper block in an Air Products displex closed-cycle helium refrigerator. The spectra were obtained by using a Spex 0.75-m monochromator, RCA C31034 photomultiplier, photon counting, and computer data collection.[9]

Lifetime measurements were carried out by monitoring the emission through the 0.75-m monochromator at two wavelengths, the first corresponding to the maximum of the emission band and the second to the long-wavelength side of the peak. The decay curves were recorded by using a Tektronix RTD 710 transient digitizer interfaced to a computer. The instrument response time was about 15 ns. The data were later transferred to a VAX780 computer for further processing.

Results

The 12 K luminescence spectra of the cube and chair isomers of $(Ph_3P)_4Ag_4I_4$ are shown in Figure 1. The emission maximum of the chair form at 23 900 cm^{-1} is at significantly higher energy than that of the cube form at 22 000 cm^{-1}. The fwhm for the chair is 2600 cm^{-1}, and that for the cube is 2900 cm^{-1}.

The temperature dependences of the emission spectra follow the same pattern for both isomers. As the temperature is raised, the emission intensities decrease and shift slightly to the red. When the temperature is raised to 120 K, for example, the emission intensities decrease by about a factor of 3 and the band maximum shifts by about 500 cm^{-1}.

Emission lifetimes were measured for both isomers at 15 K. The luminescence decay was monitored at the emission band maximum and at 18 000 cm^{-1} in the case of the cube and at the band maximum and 21 000 cm^{-1} in the case of the chair. The lifetime of the cube isomer is 40 ± 20 μs and that of the chair isomer is 300 ± 100 μs. A short-lived component of about 50 μs was observed in the latter case and is probably the result of a trace amount of the cube isomer in the crystals of the chair isomer. A very long-lived component (~ms) was observed in the decay curves of some samples. Free triphenylphosphine emits in the 23 000-cm^{-1}

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(1) Vogler, A.; Kunkely, H. *Chem. Phys. Lett.* **1989**, *158*, 74.
(2) Vogler, A.; Kunkely, H. *Chem. Phys. Lett.* **1988**, *150*, 135.
(3) Hardt, D. D.; Pierre, A. *Inorg. Chim. Acta* **1977**, *25*, L59.
(4) Vogler, A.; Kunkely, H. *J. Am. Chem. Soc.* **1986**, *108*, 7211.
(5) Kyle, K. R.; DiBenedetto, J.; Ford, P. C. *J. Chem. Soc., Chem. Commun.* **1989**, 714.
(6) Kyle, K. R.; Ryu, C. K.; DiBenedetto, J. A.; Ford, P. C. *J. Am. Chem. Soc.* **1991**, *113*, 2954.
(7) Henary, M.; Zink, J. I. *J. Am. Chem. Soc.* **1989**, *111*, 7407.
(8) Teo, B.-K.; Calabrese, J. C. *Inorg. Chem.* **1976**, *15*, 2474.
(9) Tutt, L.; Zink, J. I. *J. Am. Chem. Soc.* **1986**, *108*, 5830.

0020-1669/91/1330-3111$02.50/0

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.

Acknowledgment. This work was supported by Grant CHE88-06775 from the National Science Foundation. We thank Dr. Christian Reber for assistance with the lifetime measurements and the figure and for helpful discussions.

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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(10) Segers, D. P.; DeArmond, M. K.; Grutsch, P. A.; Kutal, C. K. *Inorg. Chem.* **1984**, *23*, 2874.

(11) Orgel, L. E. *J. Chem. Soc.* **1958**, 4186.

(12) Pedrini, C.; Jacquier, B. *Phys. Lett. A* **1979**, *69*, 457. Pedrini, C.; Chermette, H.; Gaume-Mahn, F. *J. Lumin.* **1981**, *24/25*, 213. Pedrini, C. *Solid State Commun.* **1981**, *38*, 1237.

(13) Harvey, P.; Gray, H. *J. Am. Chem. Soc.* **1988**, *110*, 2145.

(14) Payne, S. A.; Chase, L. L.; Boatner, L. A. *J. Lumin.* **1986**, *35*, 171.

(15) Barrie, J. D.; Dunn, B.; Hollingsworth, G.; Zink, J. I. *J. Phys. Chem.* **1989**, *93*, 3958.

(16) Che, C. M.; Butler, L. G.; Gray, H. B.; Crooks, R. M.; Woodruff, W. H. *J. Am. Chem. Soc.* **1983**, *105*, 5492.

(17) Shin, K.-S. K.; Barrie, J. D.; Dunn, B.; Zink, J. I. *J. Am. Chem. Soc.* **1990**, *112*, 5701.

Additions and Corrections

1991, Volume 30

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