VIBRATIONAL SPECTROSCOPY OF PARTIALLY BONDED COMPLEXES: A MATRIX ISOLATION INFRARED STUDY OF CH3CN - BF3

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The complex formed from acetonitrile and boron trifluoride has been called a "partially bonded molecule" since its B-N bond distance and N-B-F bond angle are intermediate between those characteristic of a weak, non-bonded interaction and a *bona fide* donor-acceptor bond.[a] Furthermore, complexes among this class have been shown to be quite sensitive to chemical medium, and in particular, undergo dramatic structural rearrangement upon crystallization, which includes a substantial contraction of the donor - acceptor bond. In fact, the C-N stretching frequency of $\mathrm{CH_3CN-BF_3}$ was recently observed in solid argon[b] at a value very near that of the crystalline complex.[c] This seemed to indicate that the inert matrix environment caused a nearly full contraction of the B-N dative bond. We have undertaken a re-examination of the complex, with an eye toward vibrational modes involving motion of the $\mathrm{BF_3}$ moiety, which should be rather sensitive to the effects of complexation. We have observed and identified several new absorption features in argon matrices seeded with 0.1 to 1.0 percent $\mathrm{CH_3CN}$ and $\mathrm{BF_3}$ that we assign to the 1:1 complex. The basis for these assignments is: dependence on both component species, consistent relative intensities across a wide range of conditions, and isotope shifts consistent with recent calculations[d] on the gas-phase complex. Our observations of the $\mathrm{BF_3}$ antisymmetric stretching mode (ν_{13}) indicate that, contrary to the previous study, matrix-isolated $\mathrm{CH_3CN-BF_3}$ more closely resembles the gas-phase complex than the crystalline species. Recently obtained spectra of two additional isotopic forms of the complex provide further support for our assignments, and will also be discussed.

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[c] Swanson, D. F.; Schriver, D. F. *Inorg. Chem.* **1970**, *9*, 1406.
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