The Infrared Spectrum of Hofmann's Benzene Clathrate

By S. AKYÜZ, A. B. DEMPSTER,* R. L. MOREHOUSE, and N. ZENGIN
(*Institute of Physics, Faculty of Engineering, Hacettepe University, Ankara, Turkey*)

Summary Unless sufficient care is taken in the preparation of Nujol mull or potassium bromide disc samples of Hofmann's benzene clathrate, partial decomposition occurs and spurious i.r. spectra are recorded.

HOFMANN'S benzene clathrate, $Ni(NH_3)_2Ni(CN)_4,2C_6H_6$, has been subject to numerous i.r. studies.[1-4] However, the spectra are neither entirely in agreement among themselves nor are they consistent with the spectrum expected from the structure as determined by *X*-ray diffraction.[5] In particular, two strong bands at 1230 and 1164 cm^{-1} are both attributed by Miyoshi *et al.*[4] to symmetrical bending vibrations of ammonia, whereas symmetry considerations predict only one such vibration.

We have recorded spectra in which the 1164 cm^{-1} band is the *only* NH_3 vibration of significant intensity in the 1200 cm^{-1} region. Such spectra can only be obtained by using the chemically pure clathrate which is stirred into the Nujol oil to make a mull. Unfortunately, the spectra have sloping base lines and the distorted band shapes expected from samples with large, irregular particles. These features cannot be avoided because the grinding procedure used in the normal preparation of Nujol mull samples, not to mention the grinding and evacuation involved in the preparation of KBr discs, causes decomposition of the clathrate. Benzene slowly escapes from the clathrate under low pressure. In spectra of samples evacuated before preparation of the mulls with our stirring technique, the 1230 cm^{-1} band showed a progressive increase in intensity with evacuation time, while the 1164 cm^{-1} band decreased. Some of these spectra closely resembled those previously described for the pure material.[2-4] We have thus shown that decomposition of the clathrate occurs through a loss of benzene during the normal procedures for making mulls or discs. It is now possible to assign the 1164 cm^{-1} band to the symmetrical NH_3 bending vibration in the pure benzene clathrate and the 1230 cm^{-1} band is a similar vibration arising from NH_3 not surrounded by benzene. The relative intensity of these two bands indicates the quality of the sample. Our result is applicable to studies of analogous Hofmann-type clathrates.

We thank the students of the physical chemistry laboratory for assistance with sample preparation.

(*Received, 29th November* 1971; *Com.* 2045.)

[1] E. E. Aynsley, W. A. Campbell, and R. E. Dodd, *Proc. Chem. Soc.*, 1957, 210.
[2] V. M. Bhatnagar, *Z. Anorg. Allgem. Chem.*, 1968, **363**, 318.
[3] R. S. Drago, J. T. Kwon, and R. D. Archer, *J. Amer. Chem. Soc.*, 1958, **80**, 2667.
[4] T. Miyoshi, T. Iwamoto, and Y. Sasaki, *Inorg. Chim. Acta*, 1967, **1**, 120.
[5] J. H. Rayner and H. M. Powell, *J. Chem. Soc.*, 1952, 319.