sonably assigned to the e′ → a′ d–d transition. The drop in energy of this absorption in the series FeL_5^0, CoL_5^+, NiL_5^{2+} can be taken to reflect the expected decline in ligand field contribution from metal-to-ligand π bonding. These results are consistent with the idea that the π acidity of these phosphite esters dominates the ligand field parameter *Dq* in these systems, since, in the absence of such an effect, *Dq* is expected to rise with metallic charge. The shorter wave-length of the d–d absorption for a given $P(OCH_2)_3CEt$ complex compared with that of its $P(OMe)_3$ analogue is also in agreement with the poorer Lewis basicity of the caged ligand,[13,16,17] the lower negative charge calculated for its phosphorus,[18] and hence its higher π acidity.[18]

It is interesting to note that the expected shift of $\delta(^1H)$ to lower applied field with increasing charge is also approximately linear in the series where L = $P(OMe)_3$.

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Registry No. $Fe(P(OMe)_3)_5$, 55102-04-0; $Fe(P(OCH_2)_3CEt)_5$, 61128-96-9; $[Co(P(OMe)_3)_5]BF_4$, 22323-14-4; $[Co(P(OCH_2)_3CMe)_5]BF_4$, 61128-97-0; $[Ni(P(OMe)_3)_5](BF_4)_2$, 53701-91-0; $[Ni(P(OCH_2)_3CEt)_5](BF_4)_2$, 53701-93-2; ^{31}P, 7723-14-0.

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Study of Borane Production from Pyrolyzed Diborane by Molecular Beam Velocity Analysis Spectrometry

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Diborane must rank high on the list of most heavily studied compounds.[2,3] This is not surprising considering the early interest in boron compounds as fuels. New studies have appeared in the literature as interest rekindles in boron chemistry due to the possible utilization of higher boranes and carboranes as solid propellant ballistic moderators. New methods of synthesis involving both equilibrium as well as the exciting nonequilibrium techniques involving laser photochemistry are being attempted to improve specificity and efficiency of reaction paths for these compounds which undergo complex reaction mechanisms.[4,5]

Over 25 years of controversy have been associated with the mechanism for the thermodecomposition of diborane, the simplest of the stable boranes.[6–12] All mechanisms with the exception of that proposed by Fehlner and later withdrawn[8–10] were based upon the initial production of BH_3. However, direct unambiguous proof for the formation of BH_3 during B_2H_6 pyrolysis still does not exist. Sinke et al. based their evidence for the formation of BH_3 upon the changes occurring in the low-mass (10–13) ion fragmentation pattern relative to the high-mass ion group (21–27) as determined under pyrolyzing and nonpyrolyzing conditions.[11] Fehlner and Fridman based their evidence upon the increase in the mass 14 ion signal (BH_3^+) under pyrolyzing conditions relative to that at room temperature[10] while Wilson and McGee[12] argued that changes in the ionization efficiency curves for the mass 12 and 13 ions was evidence for BH_3. Evidence such as this, while reasonable, is not unambiguous. A required assumption is that the fragmentation pattern of B_2H_6 does not change with temperature. To obviate this assumption we have restudied the pyrolysis of B_2H_6 by a fundamental method that we call modulated molecular beam velocity analysis spectrometry. This method allows differentiation of neutrals before they undergo ionization and possible fragmentation when traversing the mass spectrometer ionizer.

Experimental Section

The diborane, obtained from Callery Chemical Co., was stated to be at least 99 mol % pure at the time of shipment. Shipment at ambient temperatures and storage in a freezer between runs probably resulted in some decomposition. Careful multiple trap-to-trap distillations were made utilizing a glass vacuum manifold with traps immersed in acetone–Dry Ice, methylcyclohexane–liquid nitrogen, and liquid nitrogen. The purity of the diborane was checked with a quadrupole mass spectrometer, which is an integral part of the molecular beam apparatus. No impurities were detected under our operating conditions. The mass spectrum agreed very well with those published previously.[13]

A schematic of the molecular beam system is shown in Figure 1. The gas source was the glass vacuum manifold used for purifying the diborane. The diborane pressure and flow rate were monitored with Hasting Thermopile and Linear Mass Flow gauges in copper tubing connecting the glass manifold with the molecular beam apparatus. The pyrolysis oven was a 1-cm quartz tube packed with quartz capillaries. The oven was heated resistively by a tungsten wire wrapping. Oven temperature was measured with a thermocouple placed in the gas flow of the oven. The beam exited the oven through a 1 mm wide by 6.4 mm high slit into a high-vacuum drift space. The tuning fork modulated the beam at 504 Hz and supplied a direct reference signal for the Lock-In amplifier. The velocity selector was a duplication of that described by Grosser and was operated in the forward low-resolution (19.2%) mode for signal enhancement pur-

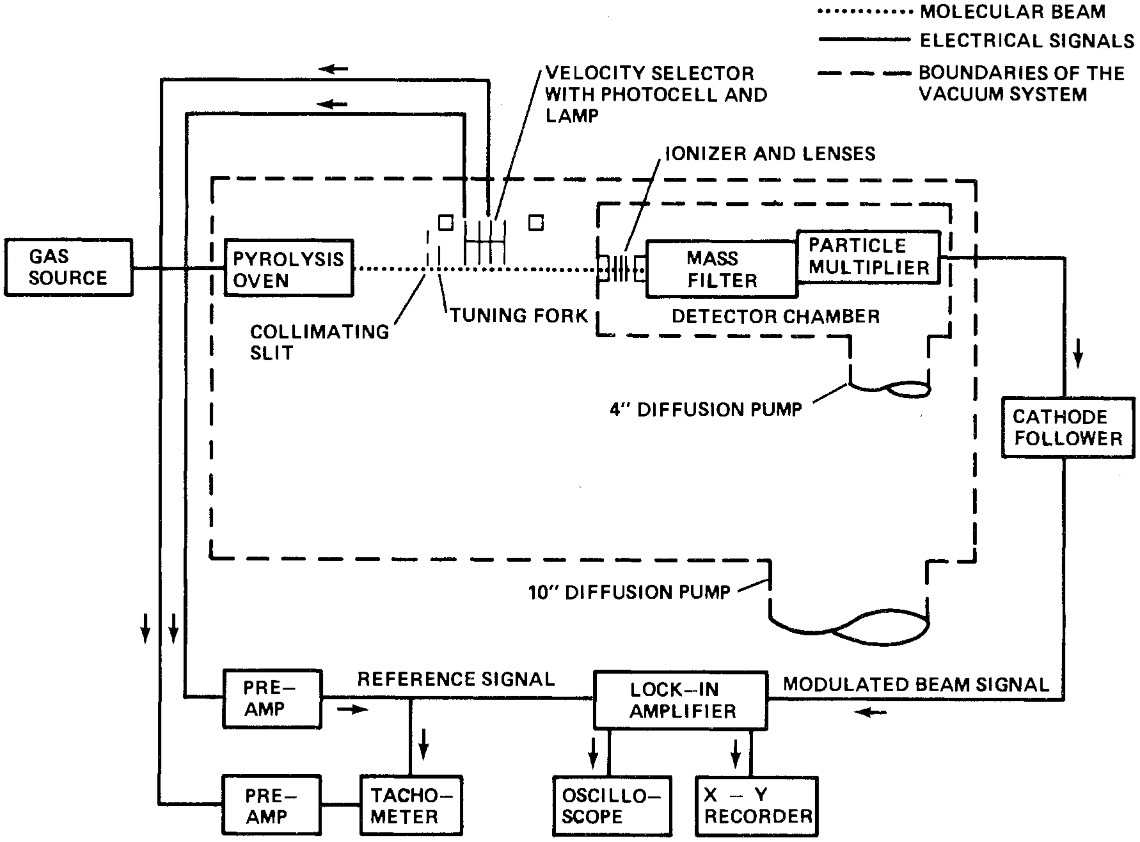

Figure 1. Block schematic of experimental apparatus.

Table I. Typical Apparatus Operating Conditions for B_2H_6 Pyrolysis

Temperature	673 K
Flow	0.5 std cm^3/min
Pyrolyzer pressure	(50–150) × 10^{-3} Torr
Main chamber pressure	5 × 10^{-7} Torr
Detector chamber pressure	2 × 10^{-8} Torr
Electron energy	50 eV

poses.[14] The frequency of the selector was monitored with a lamp, photocell and frequency counter.[15] The velocity selector was calibrated by two methods. One involved the forward–reverse method described by Grosser[14] and the other assumed a modified Maxwell–Boltzmann distribution[16] for a low-flow CO_2 beam passed through the unheated pyrolyzer beam tube. The velocity-selected beam then passed through a slit into a differentially pumped detector chamber containing the ionizer and mass spectrometer.[17] The detector chamber could be rotated off axis to monitor the background signal for comparison and returned to its original position (±0.1°) by means of an external hand-operated calibrated gear arrangement. Typical operating conditions are listed in Table I.

Results and Discussion

Figure 2 shows the un-velocity-selected mass spectrum of diborane after passing through the pyrolyzer which was heated to 673 K. Upon heating, the most noteworthy changes occur in the mass 14 and 13 peaks. At the high-temperature pyrolyzing conditions the low-mass ion group underwent an intensity change. The mass 13 peak became larger than the mass 11 peak. The mass 14 peak, although small, was generally found to have greater intensity at 673 K than at room temperature. This is in agreement with results published previously.[10-12] Ionization efficiency curves run on the mass 11, 12, and 13 peaks demonstrated greater efficiency at lower electron energies at high temperatures than at 298 K suggesting that a fraction of each of the ion signals may be originating from something other than B_2H_6. In an effort to determine if the change in the mass spectrum at high temperature was due to the production of borane or to change in the diborane fragmentation pattern, we decided to velocity-analyze the distribution of neutrals producing mass 13 and compare it to the velocity distribution of the mass 27 precursors.

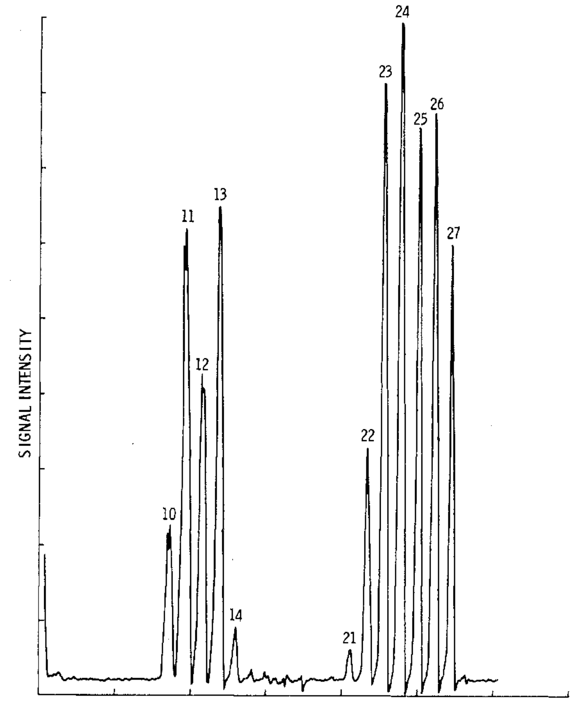

Figure 2. Mass spectrum of diborane at 673 K.

Figure 3 shows a room-temperature comparison of the velocity analysis of the neutrals which produce the mass 13 and 27 ions. The signal intensity is given in arbitrary units

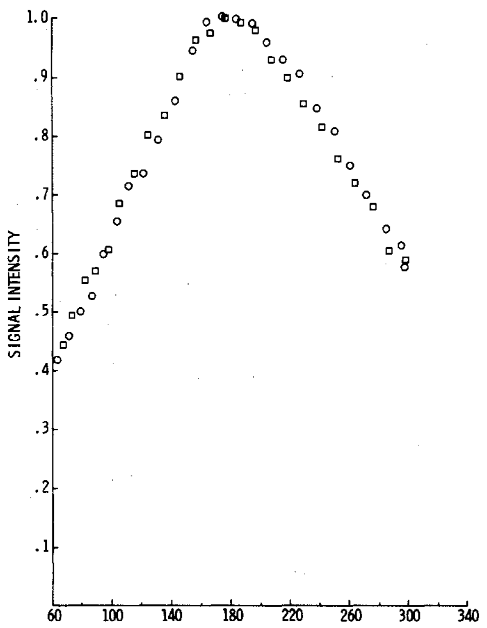

Figure 3. Comparison of velocity analysis of mass 13 (squares) and mass 27 (circles) precursors at 298 K.

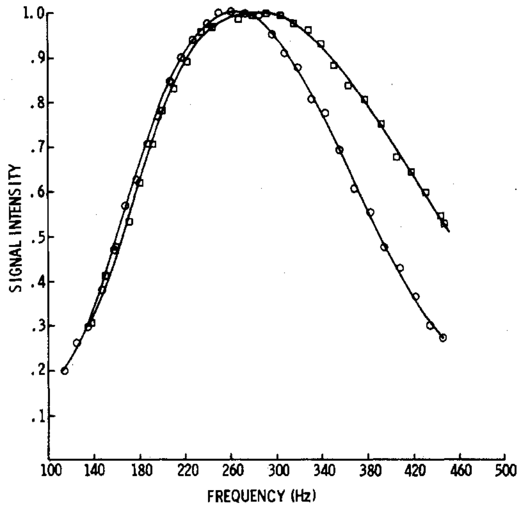

Figure 4. Comparison of experimental velocity analysis of mass 13 (squares) and mass 27 (circles) precursors at 673 K.

with the maximum normalized to unity and the frequency of the selector's rotation is directly proportional to molecular velocity. As expected there is no difference because the velocity selector is analyzing the same and only neutral precursor, B_2H_6, for production of both ions.

Figure 4 shows a typical velocity analysis at 673 K of the neutral precursors leading to mass 13 and 27 ions. The mass 13 ion has a distribution of neutrals which has a faster component than those leading to mass 27. Under these pyrolyzing conditions the mass 27 ion may only arise from undissociated B_2H_6. The only explanation for the faster neutral precursor distribution of mass 13 ions is the production of a lighter neutral fragment. This is taken as evidence for production of borane BH_3 leading to the BH_2^+ ion.

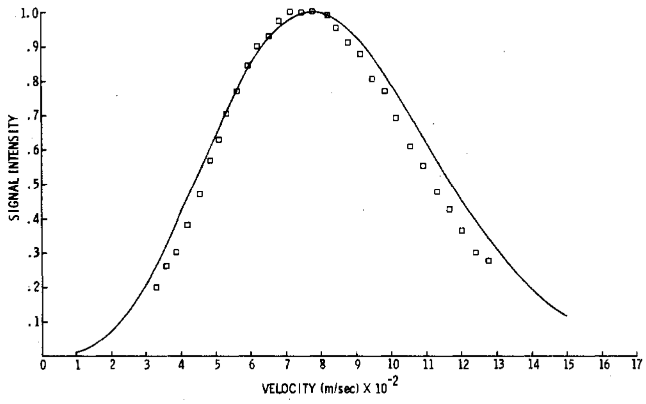

Figure 5. Comparison of the modified Maxwell–Boltzmann distribution (solid line) for a molecular beam to the experimental mass 27 precursor velocity analysis (squares) at 673 K.

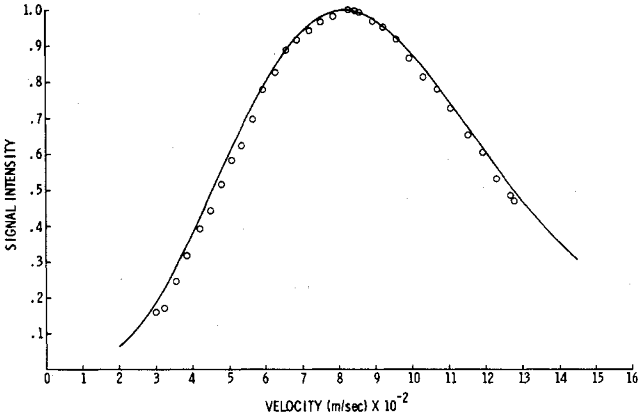

Figure 6. Fit of modified Maxwell–Boltzmann distribution for a molecular beam containing 70% mass 28 + 30% mass 14 (solid line) to one run of an experimental veloctiy analysis of mass 13 precursors (circles) at 673 K.

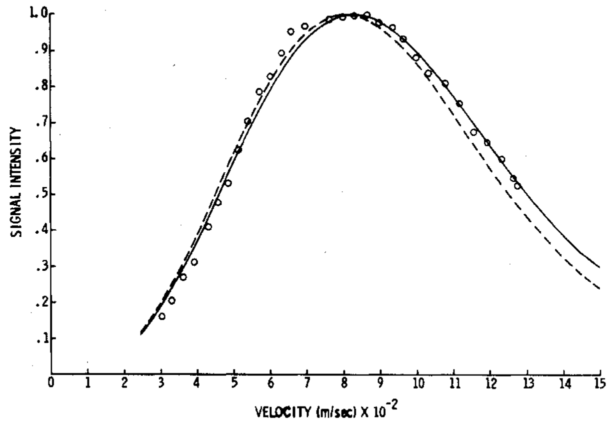

Figure 7. Comparison of 65% mass 28 + 35% mass 14 (solid line) and 75% mass 28 + 25% mass 14 (dashed line) modified Maxwell–Boltzmann molecular beam distribution fits to one run of an experimental velocity analysis of mass 13 precursors (circles) at 673 K.

Figure 5 shows a modified Maxwell–Boltzmann fit to the velocity-analyzed distribution leading to the mass 27 ion at 673 K which indicates the system is a good representation of thermoequilibrium. To determine the amount of BH_3 formed under our experimental conditions, mixed modified Maxwell–Boltzmann distribution functions were constructed, composed of fractional parts of mass 28 and 14 distributions at 673 K. Figure 6 shows an experimental fit of 70% mass 28 + 30% mass 14. Figure 7 shows a determination in which the 65% mass 28 + 35% mass 14 construction gave the best experimental fit. An attempted 75% mass 28 + 25% mass 14 fit is also included for comparison. An average of three determinations resulted in our conclusion that 32% of the mass 13 ion arises from mass 14 or BH_3. Using peak height intensities, we found that 10.9% of the ions detected at 673 K could be attributed to BH_2^+ (mass 12 and 13). Correcting for boron isotopic abundance, 8.6% of the detected ions were

BH_2^+, mass 13. Since we determined by velocity analysis that 32% of mass 13 was due to a BH_3 precursor, then 2.7% of the total material leaving the pyrolyzer is BH_3 appearing as mass 13. Mappes and Fehlner's[18] determination of the electron bombardment fragmentation pattern for BH_3 gave 56.4% as mass 13. Dividing 2.7% by this fragmentation factor leads to a total of 4.8% BH_3 production. Since the assumed mechanism is $B_2H_6 \rightarrow 2BH_3$, 2.4% of the B_2H_6 is decomposing to molecular borane at our experimental conditions. This result may be compared to that of Fehlner and Fridman,[10] who reported a maximum BH_3 yield of 0.8% at 650 K.

We have now provided unambiguous evidence for the production of borane from pyrolyzed diborane. It is also evident that the experimental technique which has been developed here has expanded the utility of the mass spectrometer for determining thermodecomposition mechanisms in the gas phase.

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Registry No. B_2H_6, 19287-45-7; BH_3, 13283-31-3.

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On the Superexchange Mechanism in Polymeric Heterocyclic Diamine Bridged Copper(II) Complexes. 2

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Within recent years numerous studies of metal complexes of pyrazine (pyr) have been described.[1-6] In spite of its low basicity ($pK_{a_1} = 0.65$[7]) pyrazine can function as a bridging bidentate ligand giving rise to dimers, e.g., $[(NH_3)_5Ru^{II}$–pyr–$Ru^{III}(NH_3)_5]^{5+}$,[5] and polymers, e.g., $[Cu(hfac)_2\cdot pyr]_n$.[4] Previously, we have examined $[Cu(NO_3)_2\cdot pyr]_n$[1-3] and related compounds[8-10] by magnetic susceptibility techniques and have shown conclusively that antiferromagnetic spin coupling is affected by way of the π system of the heterocyclic ligand. Also, Creutz and Taube[5] have observed spectroscopically an intervalence-transfer band in the mixed-valence compound $[(NH_3)_5Ru^{II}$–pyr–$Ru^{III}(NH_3)_5]^{5+}$. The fact that the π system of pyrazine provides an excellent pathway for spin–spin interactions between metal ions is well documented. It was of interest to determine the nature of the spin–spin interactions, if any, across the pyrazine bridge in $Cu(hfac)_2\cdot pyr$ and to compare the results with $Cu(hfac)_2\cdot$Dabco (Dabco = 1,4-diazabicyclo[2.2.2]octane). In the latter compound the interaction can occur only by a σ-bond mechanism. To supplement this work, the 1,5-naphthyridine complex of $Cu(hfac)_2$ was prepared and studied. The results of these studies are reported herein.

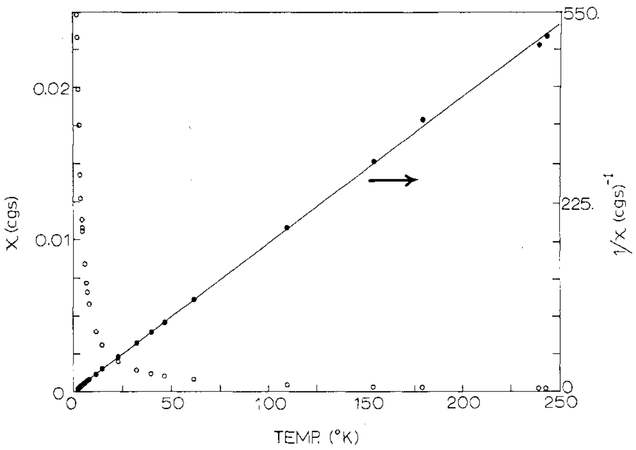

Figure 1. Magnetic susceptibility data (○) and reciprocal magnetic susceptibility (•) for the $Cu(hfac)_2\cdot pyr$ complex from 1.8 to 250 K. The solid line is the best fit of the data to the Curie–Weiss equation.

Experimental Section

All of the complexes were prepared by adding stoichiometric (1:1) amounts of ligand in tetrachloromethane to diaquobis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)copper(II), $[Cu(hfac)_2(H_2O)_2]$.[4,11] The precipitated complexes, $[Cu(hfac)_2L]_n$, were washed with tetrachloromethane and air-dried. Anal.[12] Calcd for $Cu(hfac)_2\cdot pyr$, $C_{14}H_6N_2O_4F_{12}Cu$: C, 30.15; H, 1.08; Cu, 11.4. Found: C, 29.92; H, 1.07; Cu, 11.6. Calcd for $Cu(hfac)_2\cdot$Dabco, $C_{16}H_{14}N_2O_4F_{12}Cu$: C, 32.58; H, 2.39; Cu, 10.8. Found: C, 32.48; H, 2.30; Cu, 10.7. Calcd for $Cu(hfac)_2\cdot$1,5-naphthyridine, $C_{18}H_8N_2O_4F_{12}Cu$: C, 35.58; H, 1.33; Cu, 10.4. Found: C, 35.28; H, 1.21; Cu, 10.6. Copper was determined by EDTA titration with SNAZOX indicator.[13] 1,5-Naphthyridine was prepared as described previously.[14]

Magnetic susceptibilities were determined with a Foner-type vibrating-sample magnetometer[15] operating at a field strength of 10000 G. Calibration of the magnetometer was checked using $HgCo(NCS)_4$[16] with the more recent correction to the Weiss constant[17] being applied and then recalibrated with $(NH_4)_2Mn(SO_4)_2\cdot 6H_2O$.[18] Both standards agreed within 2%. The magnetic field was calibrated as previously reported[19] and is accurate to better than 0.15% at 10 kG. Sample temperature was measured with a gallium arsenide diode that had been standardized against a commercially calibrated diode.[20] A value of 60×10^{-6} cgsu was used for the temperature-independent paramagnetism of the copper(II) ion and constituent diamagnetic corrections were estimated from Pascal's constants.[21] The EPR spectra were taken with a Varian E-3 X-band spectrometer. The magnetic field, klystron frequency, and field sweep were checked using the double standard: DPPH free radical (g = 2.0036) and vanadyl(IV) acetylacetonate in benzene.[22] Electronic spectra were obtained on a Cary 17 recording spectrophotometer using a mull (transmission) technique described previously.[23]

Results

The magnetic susceptibility data for the $Cu(hfac)_2\cdot pyr$ complex are shown as a function of temperature in Figure 1. The behavior of all three complexes is similar; the data are typical of spin $^1/_2$ paramagnets[24] and obey the Curie–Weiss