Appreciable concentrations of polyborates occur in concentrated solutions of boric acid above a pH of 6.5. The previously reported results[10] on the stabilities of the polyborates were used to take this factor into account in the calculation of the quotients in Table I.

We make the following observation about the possible occurrence of fluoropolyborates in these concentrated solutions. It is unlikely that fluoride would occur in bridging positions in polyborate structures since the complexes of fluorides with metal ions are monomeric in aqueous solutions. Also, one might expect the substitution of a fluoride for hydroxide in a terminal position of a polyborate species to occur with a stability similar to that of $BF(OH)_3^-$, *e.g.*

$$B_3(OH)_{10}^- + F^- = B_3(OH)_9F^- + OH^- \qquad \log Q \approx -0.4$$

If species do indeed exist with such stabilities, they would appear in only very minor amounts under these experimental conditions.

Chemical Shifts. The chemical shifts observed for the various compositions are given in Table II. It is interesting to compare this system with the similar fluoroberyllate species. Hogben, *et al.*,[11] observed the ^{19}F nmr spectra of the four fluoroberyllate species $BeF_x(H_2O)_{4-x}{}^{2-x}$ where x is 1-4. Each of these species gives a quartet with the chemical shifts regularly spaced at 84.8, 87.4, 89.8, and 92.4 ppm (mean positions) upfield from trifluoroacetic acid in going from BeF_4^{2-} to $BeF(H_2O)_3^+$.

Interestingly this is the reverse of the order observed for the hydroxylfluoroborates. These resonances are downfield from C_6F_6 by amounts increasing in the order (see Table II) $BF_4^- < BF_3(OH)^- < BF_2(OH)_2^- < BF(OH)_3^-$. This reversal of the shifts for the hydroxyfluoroborates from the corresponding fluoroberyllates may be due to the difference in the OH^- and H_2O as ligands, since the OH^- is expected to be more tightly bound than the H_2O. Also, the trends observed by Coyle and Stone[12] for the species BF_xY_{3-x} are similar to that observed for the fluoroborates. BF_2Cl and $BFCl_2$ are downfield from BF_3 51.5 and 99.0 ppm, respectively. Likewise, BF_2BR and $BFBr_2$ are downfield from BF_3 at 60.4 and 130.4 ppm, respectively.

Registry No. $B(OH)_3$, 10043-35-3; F_2, 7782-41-4; $BF(OH)_3^-$, 32554-53-3; $BF_2(OH)_2^-$, 32554-52-2; $BF_3(OH)^-$, 18953-00-9; BF_4^-, 14874-70-5.

Acknowledgment. We gratefully acknowledge the assistance of L. O. Gilpatrick, who provided the sample of $NaBF_3OH$ used in this work.

[10] R. E. Mesmer, C. F. Baes, Jr., and F. H. Sweeton, *Inorg. Chem.*, 11, 537 (1972).

[11] M. G. Hogben, K. Radley, and L. W. Reeves, *Can. J. Chem.*, 48, 2959 (1970).

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Photoelectron Spectra and Electronic Structure of Pentacarbonylmanganese Halides

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The photoelectron spectra of the pentacarbonylmanganese halides have previously been studied by Orchard and coworkers.[1] A parameter-free approximate molecular orbital study of this series has also been reported by Fenske and DeKock.[2] It was immediately recognized that these two independent studies agreed very closely in their interpretation of the electronic structure of these complexes. Particularly gratifying was the agreement that, within the limits of Koopmans' theorem, the sequence of the uppermost occupied orbitals in all three molecules is $8e > 7e > 2b_2$ and that 8e is primarily halogen in character. Despite this success, the molecular orbital treatment contained one feature which could not be adequately explained at the time. The treatment predicted that the $9a_1$ orbital, which is greater than 70% p_σ halogen, should lie between the primarily halogen 8e and the primarily metal 7e. In the original spectra of Orchard and coworkers, the $9a_1$ orbital was not observed or assigned.

Recently Brown and Chambers[3] have published another theoretical study of the electronic structures of the pentacarbonylmanganese–halogen molecules using the SCCC method. This method does not place the $9a_1$ orbital in the region of the 8e, 7e, and $2b_2$ ionizations. Furthermore, it reverses the order of the 7e and $2b_2$ levels and offers a completely new assignment for the ionizations in pentacarbonylmanganese iodide. The interpretation of this latter compound has played a key role in the assignment of the levels and in the assessment of their orbital per cent character (*vide infra*).

Much of the difficulty in the original ionization assignments and in the detection of the ionization from the $9a_1$ energy level was undoubtedly due to the instrumentation available. It permitted only a single slow scan across the energy region and the signal to noise ratio was such that low-intensity bands could not be readily distinguished from erratic base line characteristics. As a consequence of the molecular orbital studies of Fenske and DeKock, Orchard and coworkers initiated further studies of the photoelectron spectra of the pentacarbonylmanganese halides and identified the existence and energy placement of the $9a_1$ orbital in $Mn(CO)_5Cl$ and $Mn(CO)_5Br$.[4] Their results are in accord with the calculational predictions. With the improved instrumentation now available, we have obtained a set of well-resolved photoelectron spectra of the series $Mn(CO)_5X$, where X = Cl, Br, I, plus the spectrum of one additional compound, $Mn(CO)_4(CNCH_3)Br$, which is shown to aid greatly in a definitive assignment of the ionizations and in the interpretation of the electronic structure.

Experimental Section

Spectra were measured using a Varian IEE-15 electron spectrometer in the uv configuration. The helium source was pure to 0.0001%. Blank spectra showed no observable system contamination, and spectra of argon at high counting rate indicated no significant secondary source ionizations. Argon was used as a single internal standard. No inconsistencies have been observed when double standards were used. Sample purity was established by infrared analysis. Spectra of the halides were measured at 20–25°. The spectrum of $Mn(CO)_4(CNCH_3)Br$ was obtained at 50°. In all cases, separate spectra were measured at different time intervals until the supply of sample introduced to the spectrometer was depleted. No changes in any of the spectra were observed. Although the maximum counting rate was high (10,000–20,000 counts/sec), the technique of time

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[4] Private communication.

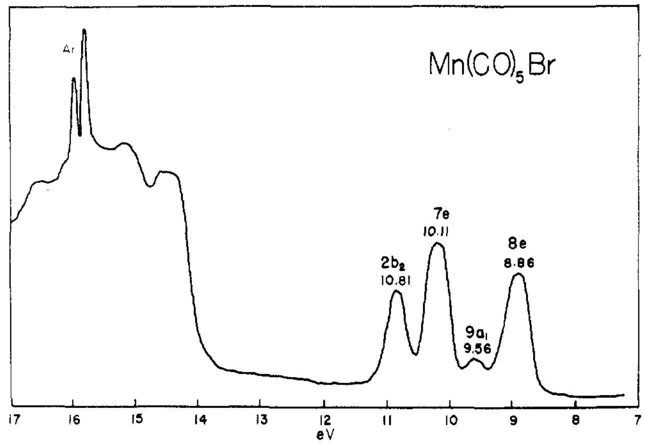

Figure 1. Full-range pe spectrum of $Mn(CO)_5Br$.

averaging proved valuable in obtaining well-defined spectra with accurately positioned peaks. A typical displayed spectrum consists of 50 individual scans of 20 sec each across the desired region. Displayed spectra are exactly as acquired by the instrument and are produced by the instrument's recorder. Peak positions were determined at their maximum.

Results and Discussion

Figure 1 shows a full spectrum of $Mn(CO)_5Br$. The major features of the pe spectra of the pentacarbonylmanganese halides have already been discussed.[1] These authors made the assignment $8e > 7e > 2b_2$ on the basis of peak intensities, assuming the ionizations of e symmetry to be approximately twice as intense as those of b_2 symmetry. Assignments based upon band intensities are subject to criticism because relative intensities are dependent on the frequency and polarization of the ionizing radiation and also on the analyzer detection angle of the ejected electrons with respect to the photon beam.[5] Nevertheless, the original assignment was in accord with the calculations of Fenske and DeKock[2] except that the latter authors predicted the presence of an additional orbital, the $9a_1$, between the two bands of e symmetry. The photoelectron cross section for an orbital of a_1 symmetry is expected to be small.[6] Figure 1 repeats the essential features of the original $Mn(CO)_5Br$ spectrum except that the additional $9a_1$ band is clearly observed and the intensity ratios differ somewhat from the original spectrum of Orchard and coworkers,[1] presumably because of the different detection angle of the Varian instrument from that employed by the original workers.

Figure 2 illustrates in more detail the ionizations from the four uppermost occupied orbitals of $Mn(CO)_5Cl$, $Mn(CO)_5Br$, and $Mn(CO)_5I$. The $Mn(CO)_5Cl$ spectrum again suggests the sequence $8e > 9a_1 > 7e > 2b_2$. In $Mn(CO)_5I$, the position of the $9a_1$ orbital is not readily apparent and no definite assignment may be made for it. While comparison with the spectra of the other two halides indicates that the $9a_1$ may be of low intensity and hidden on the low ionization energy side of the peak at 9.69 eV, peak analysis of the spectrum and the calculations of Fenske and DeKock indicate that it is on the high ionization energy side of the peak at 8.74 eV.

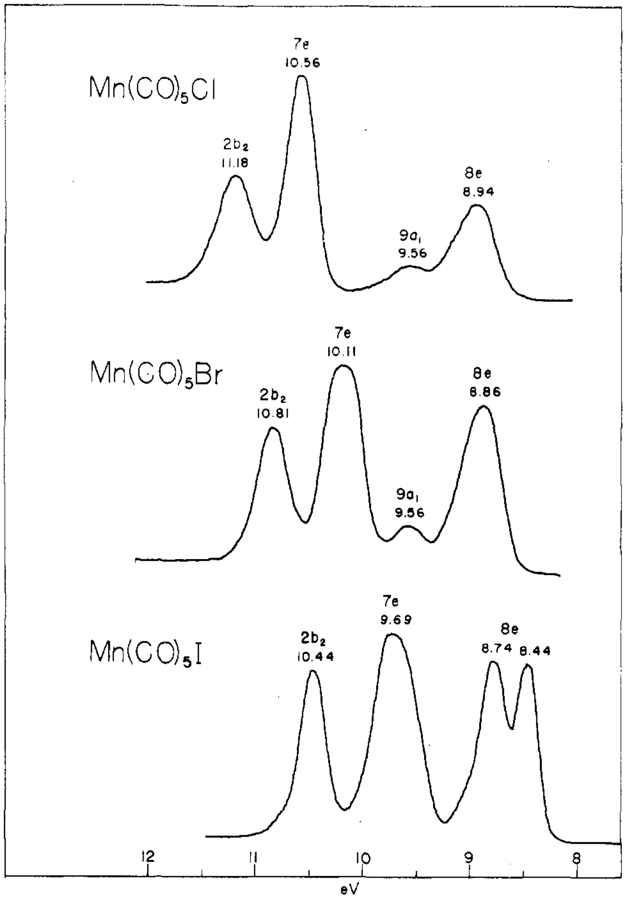

Figure 2. Metal d, halogen p region of $Mn(CO)_5X$.

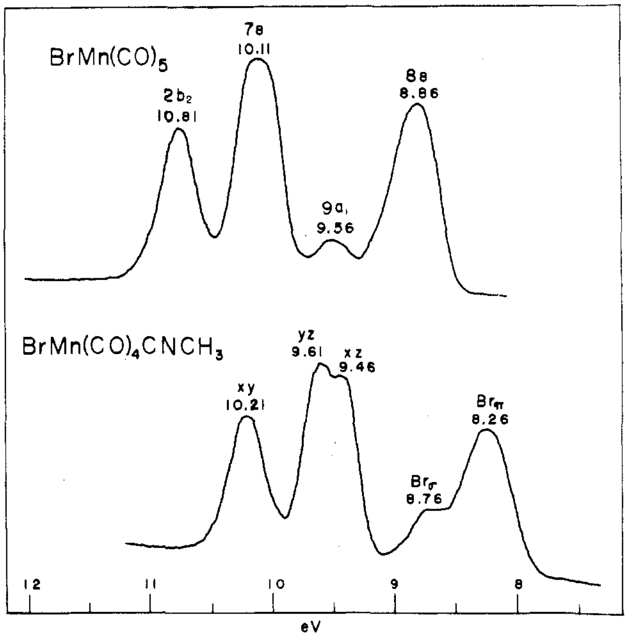

Figure 3. Metal d, bromine p region of $Mn(CO)_5Br$ and $Mn(CO)_4(CNCH_3)Br$.

The first two ionizations in the iodide are different from those observed in the bromide and chloride. The original interpretation of Evans and Orchard[1] describes an 8e orbital split by the larger spin-orbit coupling of the iodine atom. From this and the observation that the 7e does not show splitting, they concluded that the 8e is primarily halogen and the 7e is primarily metal in character.

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(5) W. C. Price, A. W. Potts, and D. G. Streets (p 197) and M. B. Robin, N. A. Kuebler, and C. R. Brundle (p 351) in "Electron Spectroscopy," D. A. Shirley, Ed., North-Holland Publishing Co., Amsterdam, 1972; J. A. Kinsinger and J. W. Taylor, *Int. J. Mass Spectrom. Ion Phys.*, in press.

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Table I

Orbital symmetry	$BrMn(CO)_5$			$ClMn(CO)_5$		$IMn(CO)_5$		$BrMn(CO)_4(CNCH_3)$		Orbital type
	Calcd	Exptl	Scale	Pred	Exptl	Pred	Exptl	Pred	Exptl	
8e	7.59	8.86	1.27	9.48	8.94	8.43	8.44–8.74	8.38 8.40	8.26	p_x p_y } halogen
$9a_1$	9.70	9.56	−0.14	10.31	9.56	8.93	9 (?)	8.87	8.86	p_σ halogen
7e	9.16	10.11	0.95	10.51	10.56	9.86	9.69	9.34 9.70	9.46 9.61	d_{xz} d_{yz} } Mn
$2b_2$	9.32	10.81	1.49	11.01	11.18	10.63	10.44	10.21	10.21	d_{xy} Mn

Brown and Chambers have offered an alternative explanation from the result of the SCCC calculation.[3] This calculation shows a nondegenerate b_1 orbital now slightly below the 8e orbital and thus now occupied, yielding a new ionization. The origin of this b_1 level is not specified in the article. Two types of b_1 orbitals appear in these molecules. The first type consists of the bonding and antibonding combinations of the equatorial CO σ orbitals with the metal $3d_{x^2-y^2}$ orbital. The second type consists of the essentially nonbonding b_1 combination of the in-plane CO 1π and 2π orbitals. It is difficult to understand the filling of either an antibonding σ combination or the virtual 2π orbitals. Moreover, if such an upper b_1 level, which is unoccupied in the chloride and bromide complexes, is filled in the iodide complex, there would be only two electrons available for the 8e level. The implications of a half-filled orbital of e symmetry do not conform to the known magnetic properties of $Mn(CO)_5I$.

The discussion to this point has admittedly been based on the appearance of the spectra and in particular on the expected relative peak intensities for orbitals of specific symmetries and degeneracies. As previously mentioned such considerations are suspect. This may be seen in Figures 2 and 3, where relative intensities vary substantially from molecule to molecule as the character of the orbital changes. More substantial evidence which does not rely upon peak intensities is offered by a theoretical and experimental study of a slightly different molecule, $Mn(CO)_4(CNCH_3)Br$.

The importance of this molecule may be seen from its expected electronic structure in relation to $Mn(CO)_5Br$. The methyl isocyanide is substituted cis to the axial Br. Recent detailed studies[7] have shown that methyl isocyanide is a much weaker π acceptor than carbonyl. The result of replacing the carbonyl by the isocyanide is to alter the local electronic symmetry about the metal atom. That is, due to the lesser back-bonding out of the metal d_{xz} orbital[8] to the weaker π acceptor, the d_{xz} orbital will be destabilized relative to the d_{yz} orbital. Thus any e orbital of $Mn(CO)_5Br$ containing substantial metal character may exhibit measurable splitting upon equatorial substitution by methyl isocyanide.

Our molecular orbital calculations were used to predict the peak positions for the spectrum of $Mn(CO)_4(CNCH_3)Br$ and in particular to predict if any splitting should be resolved. Ionization potentials from pe spectra represent the differences in energy between the ground state of the molecule and the resultant ionic configurations. Koopmans' theorem attempts to relate these differences to the eigenvalues of the ground state of the molecule. However, because electron reorientation, correlation, and other factors in the excited ion and ionization process are not taken into account, even the ground-state eigenvalues of an *ab initio* calculation are not expected to correspond closely to the ionization potentials.[9] Using Koopmans' theorem, the errors of *ab initio* calculations are often on the order of several electron volts and are dependent upon the orbital type. The eigenvalues of our approximate calculations show the same behavior. Nonetheless, the differences may be accounted for systematically in a manner analogous to that of Fenske and Hall,[10] yielding quantitative prediction of ionization potentials from approximate ground-state calculations. This method recognizes that the necessary corrections to the ground-state eigenvalues vary only slightly for orbitals of closely similar character. Thus the spectrum of $Mn(CO)_4(CNCH_3)Br$ may be predicted by coupling the calculation on this molecule with scale constants derived from the calculation and corresponding spectrum of a molecule with similar orbitals. In this case $Mn(CO)_5Br$[11] is the natural choice.

The pentacarbonylmanganese halide[12] and $Mn(CO)_4(CNCH_3)Br$[13] calculations used for these predictions have previously been completed in conjunction with separate detailed force constant and bonding studies. The transferability of the correction factors from molecule to molecule may be seen by applying the scale constants derived from $Mn(CO)_5Br$ to the chloride and iodide complexes, as listed in Table I. Exceptionally good correlation between predicted and observed ionization potentials is found for orbitals of similar character, as seen for the metal 7e and $2b_2$ ionizations in the series. When correlation between orbitals of different types is attempted, for example between orbitals of different halogens, somewhat greater deviations between predicted and observed ionization energies occur but the assignments remain unambiguous.

Table I also lists the calculated IP's for $Mn(CO)_4(CNCH_3)Br$. The ionizations from levels associated primarily with the methyl isocyanide group are calculated to be above 12 eV. The metal and halogen levels are calculated to shift to lower binding energy with respect to $Mn(CO)_5Br$. The orbital assigned as 7e in $Mn(CO)_5Br$, which the calculation shows remains predominantly metal in character upon substitution, is expected to show a splitting. The 8e orbital on the other hand is calculated as predominantly halogen in character, thus yielding only a small energy separation (0.02 eV) upon substitution, which should not be observed within the limits of present instrument resolution. As Figure 3 shows, this is indeed what was found when the spectrum was obtained. The splitting of the metal d_{xz} and d_{yz} orbitals is easily resolved. No splitting of the halogen p_π orbitals is observed. Again, the halogen p_σ orbital clearly appears between the

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(7) A. C. Sarapu and R. F. Fenske, *Inorg. Chem.*, 11, 3021 (1972).

(8) For purposes of this discussion, the coordinate system is such that the metal is placed at the origin with the halogen on the $+z$ axis and the methyl isocyanide substituted on the $+x$ axis.

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(10) M. B. Hall and R. F. Fenske, *Inorg. Chem.*, 11, 768 (1972).

(11) The halide calculations employing the method as modified for general symmetry (see ref 10) were necessarily chosen for comparison. These modifications have some minor effects on the exact placement of the eigenvalues as found in the earlier calculations restricted to C_{4v} symmetry but must be used to maintain consistency within the calculations for the purpose of correlating the shifts of IP's in these molecules.

(12) M. B. Hall and R. F. Fenske, *Inorg. Chem.*, 11, 1619 (1972).

(13) R. F. Fenske and A. C. Sarapu, to be submitted for publication.

halogen p_π and the metal orbitals, thus confirming the original predictions of Fenske and DeKock.

These results stress the importance of using molecular orbital calculations as an aid when assigning photoelectron ionizations. Furthermore, it is evident that the calculational procedure used must adhere closely to the set of criteria previously described.[14] Two specific points must be appreciated. First, eigenvalues are sensitive to any selection of parameters or approximations. If a parameter selection must be made across a series of molecules, the guidelines for this selection must be strongly consistent within the framework of the method used and must not be simply reflecting an expected behavior. Otherwise any predictive or correlative ability of the method will contain substantial uncertainty, as has been noted earlier regarding the SCCC calculation. Second, if a method uses parameters or approximations that adjust calculated eigenvalues to the binding energies found in pes, then this method is of questionable value when used for interpretation of the electronic structure and related properties of the ground state of the molecule. As discussed, a large portion of these adjustments necessarily reflects factors concerned with the state of the excited ion and ionization process and not with the electronic structure of the ground state of the molecule. These excitation effects may only be accounted for as adjustments subsequent to the results of the ground-state calculation and not in the ground-state calculation itself. This study is evidence for the value of our parameter-free molecular orbital calculations as a separate and distinct aid in the assignment and prediction of photoelectron spectra for a series of related molecules.

Registry No. $BrMn(CO)_5$, 14516-54-2; $ClMn(CO)_5$, 14100-30-2; $IMn(CO)_5$, 14879-42-6; *cis*-$BrMn(CO)_4(CNCH_3)$, 37474-14-9.

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Low-Frequency Infrared Spectra of Complexes Which Exhibit Magnetic Crossover. I. Iron(II) Complexes of 1,10-Phenanthroline and 2,2'-Bipyridine

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Transition metal complexes which exhibit magnetic spin crossover have been the subject of much recent experimental and theoretical investigation.[2-8] Previous investigators have made extensive studies of the unusual magnetic properties of the complexes $[Fe(phen)_2(NCS)_2]$, $[Fe(phen)_2(NCSe)_2]$, and $[Fe(bipy)_2(NCS)_2]$ (phen = 1,10-phenanthroline; bipy = 2,2'= bipyridine) and concluded that the temperature dependence of the magnetic moment is best explained in terms of a spin-state crossover between the high-spin ($^5T_2$) and low-spin ($^1A_1$) states.[9-11] In a previous communication, we have shown that in the case of $[Fe(phen)_2(NCS)_2]$, the Fe-N(phen) and Fe-N(NCS) stretching vibrations are highly dependent on the spin state of Fe.[12] In the present paper, we have investigated the low-frequency spectra (600-100 cm^{-1}) of $[Fe(bipy)_2(NCS)_2]$ and $[Fe(phen)_2(NCSe)_2]$ at 298 and ~100°K and $[Fe(bipy)_2(CN)_2]$ at 298°K. Because of the complexity of the spectra in this region, the metal isotope technique was employed to assign the Fe-N(bipy) and Fe-N(NCS) stretching vibrations.[13-15] Using this technique, it was possible to assign the Fe-N(bipy) and Fe-N(NCS) stretching vibrations in both the high-spin (298°K) and low-spin (~100°K) states.

Experimental Section

All the compounds were prepared by methods given in the literature. $[Fe(phen)_2(NCSe)_2]$ was prepared by method (a) of Konig and Madeja.[9] Polymorph II of $[Fe(bipy)_2(NCS)_2]$ was prepared as described by Konig, *et al.*[10] $[Fe(bipy)_2(CN)_2]$ was prepared by the method of Schilt.[16] Isotopic Fe_2O_3 (purchased from Oak Ridge National Laboratory) was reduced to metallic Fe by passing hydrogen gas over the oxide at 400°. The isotopic Fe metal was dissolved in a minimum amount of 6 *N* sulfuric acid. phen or bipy was added to the resulting $FeSO_4$ solution in a 3:1 mole ratio. The resulting complexes were then treated in the same manner as the natural-abundance complexes described previously.

The infrared spectra were recorded on Beckman IR-12 (4000-400 cm^{-1}) and Hitachi Perkin-Elmer FIS-3 (400-100 cm^{-1}) spectrophotometers. All samples were recorded as Nujol mulls on CsI (4000-400 cm^{-1}) and polyethylene (400-100 cm^{-1}) plates. The spectra were recorded at a scanning speed of 1-4 cm^{-1}/min. Reproducibility was checked by multiple scans over the desired frequency range; the average error in frequency was ±0.3 cm^{-1}. The low-temperature spectra in the 600-400-cm^{-1} region were recorded using a cold cell of standard design with liquid nitrogen as a coolant. The low-temperature spectra in the 400-100-cm^{-1} region were recorded using a standard cold cell slightly modified to fit the evacuated sample chamber of the FIS-3. Liquid nitrogen was again used as a coolant.

Results and Discussion

High-Spin Spectra. Figure 1 shows the low-frequency spectra of $[Fe(bipy)_2(NCS)_2]$, $[Fe(phen)_2(NCS)_2]$, and $[Fe(phen)_2(NCSe)_2]$ from 400 to 100 cm^{-1} at 298°K.

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