harmonic potential wells and no change in force constant between ground and excited states, the intensity of the vibronic transitions in low-temperatre luminescence depends on the overlap integrals $\langle F_0(Q_2 + \rho_i(Q_2))\,|F_n(Q_2)\rangle$. The situation is analogous to a Frank–Condon progression in an a_{1g} mode, and the combination of Q_2, Q_3 which gives rise to the Jahn–Teller distortion has a_{1g} symmetry in the lower symmetry of the distorted molecule. To calculate the relative intensity in each member of the progression we may use the formula

$$I_n = \frac{1}{n}\left(\frac{x}{3}\right)^2 I_{n-1} \qquad n = \text{number of quanta of } e_g \tag{7}$$

adapted from Ballhausen.[10] In fact we measure intensities in the progressions based on the t_{1u} and t_{2u} false origins. Since these modes are diagonal in H_{JT}, we can apply the same analysis. For $x = 3.9$, the value obtained from the quenching of spin–orbit splitting, the intensity ratios I_1/I_0 or I_2/I_1 are 1.3 and 0.85 which are in reasonable agreement with experiment. The best agreement in the case of the t_{2u} false origin is found for $x = 3.3$ giving intensity ratios 1.1 and 0.6.

The Jahn–Teller energy calculated from the observed spin–orbit splitting is 310 cm^{-1} ($x = 3.9$) and that from the intensity ratios in the e_g progression 264 cm^{-1} ($x = 3.3$). Both values are considerably larger than the spin–orbit parameters in $\hat{H}_{eff}$. This is the important consideration when treating the spin–orbit interaction as small compared to E_{JT} and justifies the approach here.

Finally, we consider the intensity in the origins. The observed oscillator strength is 5×10^{-9}. To estimate the total magnetic dipole intensity in the vibrational progressions, we multiply this by the intensity ratio between the t_{1u} and t_{2u} false origins and the progressions in a_{1g} and e_g built on them, about 1:100. The total observed magnetic dipole intensity is then about 5×10^{-7}. We can calculate the magnetic dipole intensity using the eigenvectors of the crystal field calculation. Taking the refractive index to be 1.5 and the orbital reduction factor as 0.4, a value which seems appropriate in $CrCl_6^{3-}$,[11] the calculated intensity is 6×10^{-6}. The disagreement may be in part due to the Cr^{2+} content of the crystal leading to an overestimation of the Cr^{3+} concentration. The total intensity of the $^4T_{2g}$ transition in the absorption spectrum is 2.2×10^{-5}. This value is somewhat lower than the $^4A_{2g} \rightarrow {}^4T_{2g}$ intensities usually found in octahedral chromium(III) complexes; e.g., in chrome alum, an intensity of 1.6×10^{-4} has been reported.[12] This tends to support the idea that the measured intensity may be too low.

Conclusion

We have demonstrated the existence of a Jahn–Teller interaction in the $^4T_{2g}$ state of $CrCl_6^{3-}$ in $Cs_2NaInCl_6$ by observation of a Ham effect and a progression in an e_g mode in the luminescence spectrum. As far as the relative contributions of t_{2u}, t_{1u}, and t'_{1u} modes to the vibronic intensity mechanism of the $^4A_{2g} \leftrightarrow {}^4T_{2g}$ transition are concerned, our results are in good agreement with the results of a moment analysis of MCD measurements.[1,2] On the other hand, our interpretation in terms of a Jahn–Teller effect is at variance with the current interpretation of the MCD data.[1,2] No spectra on oriented crystals have been measured, however; and the Zeeman effect is expected to be anisotropic.[3]

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Registry No. $CrCl_6^{3-}$, 15276-03-6; $Cs_2NaInCl_6$, 32201-16-4.

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Molecular Orbital Theory of Organometallic Compounds. 15.[1] A Comparative Study of Ferrocene and π-Cyclopentadienyl-(3)-1,2-dicarbollyliron

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The SCCC MO method is used to compare the electronic structures of π-cyclopentadienyl-(3)-1,2-dicarbollyliron and its carbon analogue, ferrocene. It is shown that while the bonding in ferrocene involves primarily the π orbitals of the cyclopentadienide ring, that in the dicarbollide complex involves the σ orbitals in an important role; thus, the intuitive view that the frontier orbitals on the dicarbollide ligand are directly comparable to the π orbitals of the cyclopentadienide ligand requires an important qualification. In both complexes the HOMO's have very high d_{z^2} character. In the dicarbollide complex the dianionic dicarbollide and anionic cyclopentadienide ligands donate 1.037 and 0.164 electrons to the iron(II) atom. Agreement between calculated results and experiment in closely related systems is noted.

Introduction

One of the most interesting developments in the field of organometallic chemistry has been the isolation of an extensive series of metallocarborane complexes.[2] A common feature of these complexes involves the bonding of a range of polyhedral carboranes to a transition metal via direct interaction between the metal and a nearly pentagonal open face of the carborane, e.g., as in $[Fe(C_2B_9H_{11})_2]^{2-}$. An extensive series of mixed metallocarborane complexes in which a transition metal is bonded on one side to a carborane and on the other to more conventional π ligands such as cyclopentadienyl or carbon monoxide as in $[(C_2B_9H_{11})Fe(C_5H_5)]^-$ and $[(C_2B_9H_{11})Mn(CO)_3]^-$ also exists.

In view of the extensive studies of these systems, it is surprising that little attention has been paid to detailed discussion of the bonding in the metallocarboranes and, in particular, to the similarities and differences between them and the closely related carbon analogues, e.g., ferrocene;

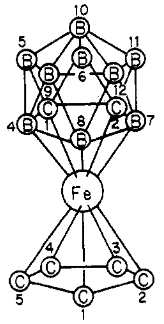

Figure 1. Conformation and atomic numbering scheme of π-cyclopentadienyl-(3)-1,2-dicarbollyliron.[11]

indeed, this is the more surprising because in one of his first papers,[3] Hawthorne rationalized the existence of metallocarboranes and the analogous metallocenes by comparing the electronic structures of the cyclopentadienide ring and $C_2B_9H_{11}^{2-}$. However, a view of the bonding has been given by Wade[4] as part of a general theory of bonding in cluster compounds, and this is very useful in providing qualitative insight into bonding. In view of the relative success of semiempirical molecular orbital methods in correlating theoretical quantities such as overlap populations, orbital energies, etc. with experimental quantities such as force constants, photoelectron spectra, Mössbauer parameters, NMR shifts, and relative reactivities,[5] we felt that it would be instructive to carry out *comparative* calculations of the electronic structures of a metallocarborane and its carbon analogue. The main purpose of the work was to examine whether indeed their electronic structures are as closely related as suggested by the above qualitative approaches and also to use the detailed theoretical comparison to draw conclusions where possible regarding experimental quantities such as the above. During the course of this work, an extended Hückel molecular orbital calculation of some icosahedral platinacarboranes appeared mainly with a view to rationalizing their observed conformations.[6]

Calculation Details

All calculations were performed according to the SCCC method[5] with self-consistency on all atoms using an AO basis throughout. The transition-metal *basis* set consisted of 3d, 4s, and 4p atomic orbitals, while the non-transition elements contained the valence shell AO's. The transition-metal atomic orbitals were represented by multi-Slater-type orbital (STO) expansions using the coefficients and exponents of Richardson and co-workers.[7] The main-group elements were represented by single STO's with exponents according to Clementi and Raimondi.[8] The diagonal Hamiltonian elements were calculated using VOIP's as determined by Basch, Viste, and Gray.[9] The off-diagonal Hamiltonian elements were calculated according to the Wolfsberg–Hehmholz approximation with $K = 1.75$. The geometry of ferrocene $FeCp_2$ was taken from the electron diffraction study by Bohn and Haaland,[10] while that for the metallocarborane $[CbFeCp]^-$ was taken from an x-ray study by Zalkin et al;[11] in both compounds the iron atom is flanked by two eclipsed pentagonal faces. The geometry of $[CbFeCp]^-$ was not idealized, so that the open pentagonal face of the carborane diverged from strict planarity. The iron–carbon and iron–boron separations are 2.04 and 2.09 Å respectively.

Discussion

Ferrocene. In an SCF Xα calculation on ferrocene,[12] the following order of upper filled and lowest empty MO's was obtained in D_{5h} symmetry: $e_1'(\pi\text{-Cp}) < e_1''(\pi\text{-Cp}) < e_2'(3d) < a_1'(3d) < e_1''^*(3d)$. Our SCCC results are in good agreement with this sequence with the two highest occupied molecular orbitals ($3e_2'$ and $4a_1'$) being essentially pure metal d orbitals. The order $3e_2' < 4a_1'$ is essential for the correct interpretation of the d–d optical absorption spectrum of ferrocene although a reverse order had been inferred from an erroneous assignment of the photoelectron spectrum based on integrated peak areas.[13] For the remaining occupied MO's there is also general agreement between the two methods, and those orbitals which are associated with the strongest metal–ring bonding all involve π orbitals of the Cp ring (namely, $3e_1''$, $3e_1'$, $3a_2''$, and $3a_1'$). There is also some contribution from the σ framework as reflected by a bonding interaction between the metal $d_{x^2-y^2}$ and d_{xy} orbitals and the ring $e_2'(\sigma)$ orbitals; nervertheless, the predominant interactions in ferrocene involve the ring π orbitals. Lists of the percentage atomic characters in the molecular orbitals of the cyclopentadienide anion and of ferrocene are available as supplementary material.

The Carborane Ligand. The dicarbollide dianion, $C_2B_9H_{11}^{2-}$ (with C_s symmetry), has 24 filled MO's. The closed-shell configuration for $C_2B_9H_{11}^{2-}$ (C_s symmetry) is $(1a')^2(2a')^2(1a'')^2(3a')^2(2a'')^2(4a')^2(3a'')^2(5a')^2(6a')^2(4a''(\pi))^2(7a')^2(8a'(\pi))^2(5a''(\pi))^2(9a'(\pi))^2(10a'(\pi))^2(11a')^2(12a')^2(6a''(\pi))^2(7a''(\pi))^2(13a'(\pi))^2(8a'')^2(14a')^2(9a'')^2(15a')^2(10a''(\pi))^2(16a'(\pi))^0$, where the symbol π denotes a high pπ density on the open face. A list of the percentage atomic characters of the frontier orbitals of the dicarbollide dianion is available in the supplementary material. The SCCC calculations support the analogy between the cyclopentadienide anion and the dicarbollide dianion insofar as the occupied MO's of the latter are of $a_2''(\pi)$, $e_2''(\pi)$ symmetry with a LUMO of $e_2''(\pi)$ symmetry. This simple qualitative reasoning was the initial inspiration for Hawthorne as mentioned in the Introduction but the analogy is tenuous in that the $a_2''(\pi)$ and $e_1''(\pi)$ of Cp^- are genuine frontier orbitals, i.e., lying high in energy, whereas their counterparts on the dicarbollide dianion or isoelectronic boron hydride lie much lower in energy than the HOMO, although the match in energy between the Cp^- and Cb^{2-} orbitals is closer than if the latter occupied the energy range close to the HOMO. Too close an analogy with the cyclopentadienide anion could not be expected in view of the obvious differences in hybridization (as reflected in the input geometry) of atoms on the open pentagonal face of the dicarbollide ligand in contrast with the near-planarity of the hydrogen atoms in the cyclopentadienyl ring in ferrocene. In fact, the reduction to C_s symmetry gives rise to MO's with a high π-percentage content which is unevenly partitioned into olefinic carbon π, allylic boron π, and mixed carbon–boron π parts.

π-Cyclopentadienyl-(3)-1,2-dicarbollyliron, $[CpFeCb]^-$. There are 40 occupied molecular orbitals in this complex and the electron configuration (labeled in C_s symmetry) is $(1a')^2(2a')^2(3a')^2(1a'')^2(4a')^2(2a'')^2(5a')^2(3a'')^2(6a')^2(7a')^2(4a'')^2(5a'')^2(8a')^2(9a')^2(6a'')^2(10a')^2(11a')^2(12a')^2(7a'')^2(13a')^2(14a')^2(15a')^2(16a')^2(17a')^2(8a'')^2(18a')^2(9a'')^2(10a'')^2(19a')^2(11a'')^2(20a')^2(21a')^2(12a'')^2(13a'')^2(22a')^2(14a'')^2(23a')^2(24a')^2(15a'')^2(25a')^2(16a'')^0(26a')^0$. Again the percentage atomic characters of the constituent ring orbitals and metal orbitals in the above molecular orbitals of $[CpFeCb]^-$ are listed in the supplementary material together with a detailed interaction diagram.

Comparison of Bonding in $FeCp_2$ and $[CpFeCb]^-$. Concentrating attention on the five highest occupied orbitals of both compounds, the following comparison of the bonding can be made. First, both compounds contain a HOMO of very high $3d_{z^2}$ content. Second, the composition of the next four orbitals in both compounds shows an important difference. In $FeCp_2$, the second and third orbitals, $e_2'(3d)$, have a very high

Table I. Total Populations

	Cyclopentadienyl Ligand		
$C_5(\sigma)$	15.300 (14.748)[a]	$C_5(\pi)$	5.487 (6.000)
	Dicarbollide Ligand		
$C_2B_3(\sigma)$	13.934 (14.338)	$B_5(\pi)$	2.735 (2.725)
$C_2B_3(\pi)$	3.445 (3.445)	$B_{10}(\sigma + \pi)$	2.940 (2.990)
$B_5(\sigma)$	12.447 (12.758)		
	Total Electron Charges (Hydrogen Included)		
Dicarbollide ligand	46.963 (48.000)		
Cyclopentadienyl ligand	25.836 (26.000)		

[a] Free ligand values in parentheses.

Table II. Atomic Charges in $[CpFeCb]^-$ and in Free Ligands

	Complex	Ligand		Complex	Ligand
		Dicarbollide Atoms			
$C_{1(2)}$	−0.105	−0.179	$B_{5(11)}$	−0.031	−0.088
$B_{4(7)}$	−0.049	−0.129	$B_{9(12)}$	−0.061	−0.131
B_8	−0.071	−0.163	B_{10}	0.061	0.011
B_6	0.002	−0.045			
		Cyclopentadienide Atoms			
C_1	−0.157	−0.150	$C_{3(4)}$	−0.158	−0.149
$C_{2(5)}$	−0.157	−0.150			

$d_{x^2-y^2}/d_{xy}$ content (91.8%) and the fourth and fifth orbitals, $e_1''(\pi\text{-Cp})$, involve extensive mixing between the ring π orbitals and the metal d_{xz}/d_{yz} orbitals (32.5%). In contrast, in $[CpFeCb]^-$, the second and third orbitals (15a″ and 24a′) involve mixing between metal d_{xy}/d_{yz} and d_{z^2}/d_{xz} orbitals (24.9 and 36.4%, respectively) with the dicarbollide orbitals having largely σ character. For the mixed $[CpFeCb]^-$ complex, it is the fourth and fifth orbitals which have very high metal content (92.2 and 82.8%). This difference in bonding pattern is important and is repeated in other interactions, such that one can conclude that the predominant interactions between the iron atom and the dicarbollide dianion involve σ orbitals on the dicarbollide whereas the predominant interactions between the iron atom and the cyclopentadienide anion involve π orbitals of the latter (see Tables I and II). Table I shows the orbital populations and total charges on the ligands in the $[CpFeCb]^-$ complex with free ligand values being given in parentheses. On complexation of the dicarbollide dianion there is a net loss of 1.037 electrons involving a reduction of electron density on all three sites, the ring open face, the closed face, and the apex, with the greatest proportional change being on the open face. In contrast, the cyclopentadienide anion loses only 0.164 electrons. It is also interesting that the cyclopentadienide anion actually gains σ-electron density on complexing which is more than compensated by the loss of π-electron density (Table I), whereas, treating the open (C_2B_3) face of the dicarbollide dianion as a quasi-pentagonal moiety, the σ-electron density decreases while the π-electron density is unchanged (Table I). The net charges on the iron atoms in the two complexes are very similar, that is, 0.748 in $FeCp_2$ and 0.800 in $[CpFeCb]^-$. The first ionization potential of ferrocene is calculated to be 9.68 eV, considerably greater than that of the complex anion, that is 7.45 eV.

Comparison with Experiment. Unfortunately, no physical measurements have been reported for $[CpFeCb]^-$ with which to compare our theoretical results but results for closely related complexes are available. For example, Wiersema and Hawthorne[14] studied electron delocalization in paramagnetic metallocarboranes of the type $(C_2B_nH_{n+2})M(C_5H_5)$ and $M(C_2B_nH_{n+2})_2$, where M = Cr(III), Fe(III), Ni(III), and Co(II) and n = 9, 8, 7, and 6.[16] These workers determined a number of salient trends.

(*i*) The mode of electron delocalization is primarily ligand to metal except for icosahedral Co(II) where the opposite holds.

(ii) The extent of delocalization in metallocarboranes is minimal and is primarily localized on the open face.

(iii) The magnitude and direction of isotropic shifts of the metallocarboranes and metallocenes (^{13}C shift only) are very similar. This result implies that the energetics of the metal–ligand interactions are similar, i.e., that the highest filled MO's are primarily metal centered and nonbonding in nature.

(iv) The variation in the isotropic coupling constants is indicative of a σ-type delocalization mechanism in that only atoms directly bonded to the paramagnetic center exhibit a large shift in their nuclear resonances.

The above results are in substantial agreement with our theoretical conclusions, especially the last point where the difference from metallocenes is highlighted; that is, in metallocenes π delocalization is predominant while in metallocarboranes the σ delocalization is more important. It is also encouraging that the pattern of filled MO's deduced from the EPR results agrees with our theoretical scheme for the highest occupied orbitals.

In an NQR study of the bonding in $Cs[(1,2\text{-}C_2B_9H_{11})_2Co^{III}]$ and $Fe(C_5H_5)_2$, Harris[15] concluded, first, that one electron of the dinegative dicarbollide ligand is localized on the open face while the other electron is partitioned over the remainder of the boron polyhedron and, second, that the 1, 2 carbons and the 4, 7, 8 borons are practically identical in their bonding to the transition metal because of the small asymmetry parameters.

Our calculations support the second conclusion, for in the case of $[(C_2B_9H_{11})Fe(C_5H_5)]^-$, if one considers the alteration in charge on the open face atoms upon complexation, the ΔQ_A values (i.e., changes in atomic charge) are 0.073, 0.080, and 0.098 for atoms $C_{1(2)}$, $B_{4(7)}$, and B_8, respectively (see Table II). However, our calculations do not support the first conclusion for $[CpFeCb]^-$; the electron delocalization calculated on the open face and on the remainder of the polyhedron framework atoms only is 0.379 (0.784) and 0.183 (0.483), respectively; it is noticeable that the hydrogen atoms take up an appreciable part of the excess charge in nearly all cases.

We now return to one of the main aims of the paper, namely, to determine to what extent detailed comparative molecular orbital calculations support the qualitative view of the bonding in metallocarboranes. The original suggestion by Hawthorne[2] that a transition metal could bond to the open near-pentagonal face of a carborane in a similar way to the bonding of the metal to a cyclopentadienyl ring is shown to be correct but with one important qualification, inasmuch as the predominant interaction involves σ orbitals of the dicarbollide which are nevertheless of the same symmetry type as the π orbitals of the Cp^- ring. The pattern of upper filled orbitals in the two complexes neatly reflects both this difference and the close similarity of the systems as witnessed by the presence of three essentially pure metal orbitals in the upper occupied regions in both cases.

Finally, it is illuminating to consider the electron counting schemes proposed by Wade[4] and Hawthorne[3] which determine the type of triangular-faced geometry a borane or carborane will assume. The dicarbollide ligand $C_2B_9H_{11}^{2-}$ belongs to the family of nido species with a geometry based on the 12-vertex icosahedron (one more than the number of framework atoms) while it has 12 + 1 electron pairs to use in skeletal bonding. If $[(C_2B_9H_{11})Fe(C_5H_5)]^-$ is visualized as being formed from $C_5H_5Fe^+$ and $C_2B_9H_{11}^{2-}$, the iron-containing moiety is found to have three orbitals and zero electrons for bonding in agreement with ref 4. From the relative positions of the HOMO's and the LUMO's it follows that electron density will flow from $C_2B_9H_{11}^{2-}$ toward $C_5H_5Fe^+$. On the iron–cyclopentadienyl fragment, the first three unoccupied MO's are of

$4e_1$ and $5a_1$ symmetry type, which are symmetry compatible to partake in bonding with the uppermost occupied orbitals of $C_2B_9H_{11}{}^{2-}$, i.e., MO's 8a″, 14a′, 9a″, and 15a′ which have masked e_1 symmetry. The three HOMO's of $C_5H_5Fe^+$, i.e., $4a_1(d_{z^2})$ and $3e_2(d_{xy}, d_{x^2-y^2})$, are symmetry incompatible; therefore, involvement in bonding with the HOMO's of the $C_2B_9H_{11}{}^{2-}$ moiety is disallowed, and, not surprisingly, they transform into MO's in the $[(C_2B_9H_{11})Fe(C_5H_5)]^-$ complex which possess very high metal orbital coefficients. The ordering of the frontier orbitals on $C_5H_5Fe^+$ agree with the description in Figure 2 of the paper of Hoffmann and coworkers.[16] Nevertheless, the essentially qualitative approaches have been and will continue to be of great use in rationalizing a large number of diverse structures.

Registry No. π-Cyclopentadienyl-(3)-1,2-dicarbollyliron, 37185-23-2; ferrocene, 102-54-5.

Supplementary Material Available: Lists of percentage atomic characters of the molecular orbitals of the cyclopentadienide anion, ferrocene, the dicarbollide dianion, and π-cyclopentadienyl-(3)-1,2-dicarbollyliron and interaction diagrams (11 pages). Ordering information is given on any current masthead page.

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Resonance Raman Spectra and Structure of the Vapor Complexes Formed by $CuCl_2(g)$ and $LCl_3(g)$ (L = Al, Ga, In)[1]

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The Raman spectra of the vapor complexes $CuAl_2Cl_8$, $CuGa_2Cl_8$, and $CuInCl_5$ are presented. Assignments of the Raman lines are obtained by isotopic substitution and by interpretation of the resonance Raman effect. On the basis of the spectral data, a structure containing a triply coordinated copper(II) ion is proposed for all three complexes.

Introduction

It is known that metal halides form complexes with group 3A metal halides in the vapor phase by reaction A,[2,3] where

$$MCl_2(s) + xLCl_3(g) \rightleftharpoons ML_xCl_{3x+2}(g) \qquad \text{(A)}$$

M is a bivalent metal ion and L is Al, Ga, or In. As a consequence of this complex formation, the volatility of the bivalent metal chloride is enhanced by several orders of magnitude. The thermodynamics and stoichiometry of this reaction have been studied by different techniques.[4] These studies showed that for L = Al, mainly 1:2 complexes are formed ($x = 2$).[2b,4] Only recently, detailed studies by visible spectroscopy revealed 1:1 ($MLCl_5$) and 1:2 (ML_2Cl_8) complexes for L = Ga and In.[5,6] The ratio between the two complexes is mainly controlled by the degree of dimerization of $LCl_3(g)$. As $AlCl_3$ exists below 500 °C mainly as a dimer, it is not surprising that only the 1:2 complexes could be observed.

The main experimental information on the structure of the vapor complexes has until now been the d–d transitions of the bivalent transition-metal ion. There is, however, no agreement on the interpretation of these spectra.[4,7–9] Emmenegger[2a] was able to rationalize the thermodynamic data of vapor complex formation assuming a structure with the transition-metal ion in a tetrahedral coordination sphere. Because Raman spectroscopy has already been used successfully to elucidate the structures of gaseous compounds at high temperatures,[10] we decided to use this method to determine the structure of the vapor complexes. One disadvantage of this method, however, is that the Raman spectrum of the vapor complex is overlapped by the spectrum of $LCl_3(g)$, always the major component of the equilibrium gas phase. As the transition-metal chloride complex is the only absorbing species in the visible and near-UV region, its Raman spectrum might under favorable conditions be largely enhanced by a resonance Raman effect. Therefore, the vapor complexes of $CuCl_2$, which show strong absorptions close to the lines of an argon ion laser, have been chosen to be studied first. A further advantage of this system is the high volatility of $CuCl_2$,[11,33] which allows one to observe the vapor complexes at temperatures of 250–350 °C for L = Al[2a] and Ga.[6]

Experimental Section

Chemicals. $CuCl_2 \cdot 6H_2O$ (p.a.) was dehydrated by refluxing in freshly distilled $SOCl_2$[12] and purified by chemical transport with $AlCl_3$. Anal. Calcd: Cu, 47.26; Cl, 52.74. Found: Cu, 47.12; Cl, 52.39. $AlCl_3$ was purified by sublimation from a mixture of 90% $AlCl_3$ (Fluka AG, purum) and 10% charcoal.[4] $InCl_3$ (Fluka AG, puriss) was sublimed under high vacuum before use. We thank Alusuisse AG, Neuhausen, Switzerland, for donating $GaCl_3$ (puriss). ^{63}CuO (^{63}Cu 97.8%) was purchased from Schenker Co.; ^{65}CuO (^{65}Cu 99.7%), from ORNL, Oak Ridge, Tenn. Professor E. Schumacher, University of Bern, Bern, Switzerland, generously provided 250 mg of $Al^{35}Cl_3$ (^{35}Cl 99%) and 250 mg of $Al^{37}Cl_3$ (^{37}Cl 99%).

Sample Preparation. A furnace fitting in the sample illuminator of the Spex Ramalog 4 was constructed (Figure 1).[13] The furnace can be closed at both ends by isolating stoppers fitted into the Pyrex tube (A). The temperature is controlled by a Eurotherm controller

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