about the chromium–arene bond in these complexes is most likely not obtained and that the complexity of the aromatic proton resonance in such complexes is the result of differences in the magnetic environment already present in the free arene.

Experimental Section

Proton magnetic resonance spectra (Table II) were obtained with a Varian Associates A-60 spectrometer using *ca.* 5–10% solutions of the complex in carbon tetrachloride containing a small amount of tetramethylsilane as an internal standard in 5-mm o.d. Pyrex tubes sealed under nitrogen.

Elemental analyses were performed by Dr. S. M. Nagy, Microchemical Laboratory, MIT, and melting points are uncorrected. Chromium hexacarbonyl was vacuum sublimed before use. *p*-Bis(trimethylsilyl)benzene was prepared in these laboratories by D. R. Blank. *p*-Diisopropylbenzene and *p*-di-*t*-butylbenzene were purchased from Aldrich Chemical Co.

The complexes (Table I) of the *para*-disubstituted arenes were prepared by heating a mixture of chromium hexacarbonyl (10 mmol) with a slight excess of the arene in diglyme to reflux for 24–30 hr following the method of Nicholls and Whiting.[5] The yellow crystalline products were initially purified by recrystallization from diisopropyl ether under nitrogen, followed by vacuum sublimation (50–80° (0.07 mm)). The preparation of the complexes of the phenyltrimethyl group IVb derivatives has been reported previously.[3]

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Contribution from the Department of Chemistry,
University of Virginia, Charlottesville, Virginia,
and the Department of Chemistry, University of
Southern California, Los Angeles, California

Magnetic Circular Dichroism of Charge-Transfer Transitions in $SbCl_6^-$ and $SnCl_6^{2-}$

By P. N. Schatz,[1] P. J. Stephens,[2] G. N. Henning,[1]
and A. J. McCaffery[1]

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In recent articles[3–8] the value of magnetic circular dichroism (MCD) in the assignment of allowed transitions has been discussed and illustrated. Its application is most clear-cut when use is made only of the qualitative dispersion form or sign of the MCD; greater ambiguity exists when finer quantitative considerations are introduced. So far, assignments based on the sign of the MCD have been limited to cases where *C* terms—originating in ground-state angular momentum—are dominant, namely $Fe(CN)_6^{3-}$,[4,5] IrX_6^{2-} (X = Cl, Br),[7] and Tm^{2+}–CaF_2.[8] *A* terms—arising from both ground- and excited-state angular momentum—have been used, by their very existence, to prove excited-state degeneracy,[6] but no assignments have been made on the basis of their signs. We present here such an application in assigning the lowest charge-transfer transitions of $SbCl_6^-$ and $SnCl_6^{2-}$.

The molecular orbital diagram generally adopted for O_h metal hexachloride complexes is shown in Figure 1.[9] The approximate magnitudes of the $t_{1u}(\pi)$–t_{2g}, $t_{2u}(\pi)$–t_{2g}, $t_{1u}(\sigma)$–t_{2g}, and t_{2g}–e_g separations are known for several d^n ($0 \leqslant n \leqslant 6$) complexes from analyses of their spectra.[7,9–11] On the other hand, little is known about the unfilled orbitals immediately above e_g or about the molecular orbital energies in complexes with more than six d electrons. Even the ordering may there be different; thus, it is not impossible in d^{10} complexes for the $t_{1u}(\pi)$, $t_{2u}(\pi)$ levels to lie above t_{2g}.

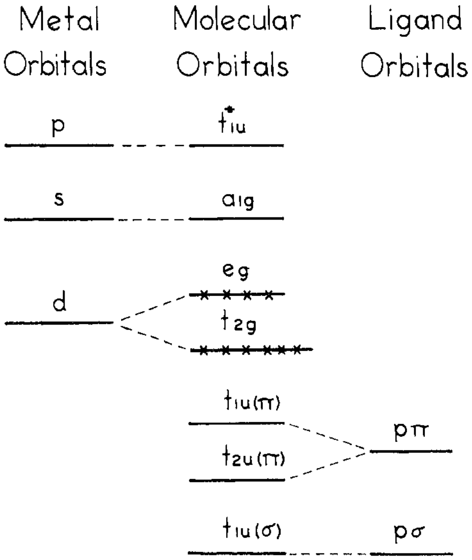

Figure 1.—Schematic molecular orbital diagram for O_h metal hexachloride complexes. Ligand g states are omitted since they are irrelevant to the present application. Crosses denote electrons in ground configuration of d^{10} complexes.

In the absence of spin–orbit coupling, the ground state of a d^{10} complex is $^1A_{1g}$ and allowed electric dipole transitions require a $^1T_{1u}$ upper state. The lowest energy one-electron excitations giving $^1T_{1u}$ levels are either $t_{1u}(\pi) \rightarrow a_{1g}$ or $e_g \rightarrow t_{1u}^*$, depending on the quantitative disposition of the energy levels. The $t_{2u}(\pi) \rightarrow a_{1g}$ transition is forbidden; hence the next allowed ligand to metal transition after $t_{1u}(\pi) \rightarrow a_{1g}$ is $t_{1u}(\sigma) \rightarrow a_{1g}$. If spin–orbit coupling is introduced, transitions become allowed to any T_{1u} spin–orbit

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[1] University of Virginia.

[2] University of Southern California.

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state—and hence to the "triplet" $t_{1u}(\pi)^5a_{1g}$, $t_{2u}(\pi)^5a_{1g}$, and $e_g{}^3t_{1u}{}^*$ levels—in proportion to the magnitude of the spin–orbit coupling.

The d^{10} complexes $SbCl_6{}^-$, $SnCl_6{}^{2-}$, and $PbCl_6{}^{2-}$ exhibit moderately intense absorption bands (ϵ_{max} ~8000–30,000) at 37,000, 45,000 and 33,000, 48,000 cm^{-1}, respectively.[9,12–15] These must be attributed to allowed transitions and are of appropriate intensity for spin-allowed charge-transfer excitations. Jørgensen[9,14] has assigned the lowest bands in all three complexes to $t_{1u}(\pi) \rightarrow a_{1g}$ and the second $PbCl_6{}^{2-}$ band to $t_{1u}(\sigma) \rightarrow a_{1g}$. $e_g \rightarrow t_{1u}{}^*$ transitions are eliminated on the grounds that the lowest allowed transitions of $PbCl_6{}^{4-}$ are in the near-uv,[13,16] that these must be attributed to $a_{1g} \rightarrow t_{1u}{}^*$, and hence that $e_g \rightarrow t_{1u}{}^*$ must lie in the far-uv. The separation of the two $PbCl_6{}^{2-}$ bands is consistent with the observed 12,000-cm^{-1} $t_{1u}(\sigma) - t_{1u}(\pi)$ separation in $IrCl_6{}^{2-}$.[7]

The absorption spectra and MCD of $SbCl_6{}^-$ and $SnCl_6{}^{2-}$ are shown in Figure 2. The similarity of the MCD in the two complexes strongly points to a common origin for the absorption bands. If it can be assumed that only one excited T_{1u} state contributes to the band, the change in sign of the MCD (associated with an A term) is attributable to the angular momentum—and hence magnetic moment—of the degenerate upper state. The great width of the bands (at half-height ~6000 cm^{-1}) is actually somewhat suggestive of overlapping transitions. However, in these complexes (though not necessarily in $PbCl_6{}^{2-}$) spin-forbidden transitions are probably not of significant intensity, and, in the absence of evidence to the contrary, we shall assume that only one transition is in fact present.

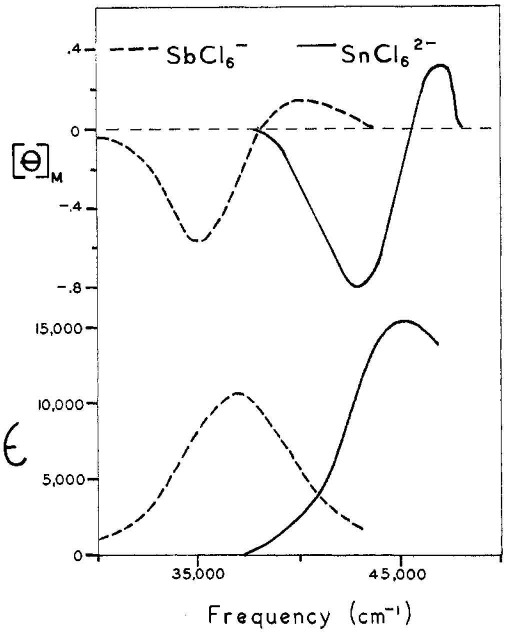

Figure 2.—Absorption spectrum and MCD of $SnCl_6{}^{2-}$ in 12 N HCl (solid line) and $SbCl_6{}^-$ in 12 N HCl (dashed line). $[\theta]_M$ is the molar ellipticity (defined as in natural optical activity) per gauss in the direction of the light beam. Absorption spectra were obtained with a Cary 14. MCD were measured as described in ref 5. The sharp cutoff of the $SnCl_6{}^{2-}$ spectrum is the result of strong solvent absorption.

We then wish to calculate the magnetic moment of the excited state for the two alternative excitations—$t_{1u}(\pi) \rightarrow a_{1g}$ and $e_g \rightarrow t_{1u}{}^*$.[17] If spin–orbit coupling is small so that we can approximate the excited state by a $^1T_{1u}$ function, the magnetic moment arises entirely from orbital angular momentum and is proportional to $\langle {}^1T_{1u}x|L_z|{}^1T_{1u}y\rangle$, where $T_{1u}x$ and $T_{1u}y$ functions transform like x and y, and $\mathbf{L}$ is the total orbital angular momentum operator. Adopting single-configuration MO wave functions, $\langle {}^1T_{1u}x|L_z|{}^1T_{1u}y\rangle$ reduces to the one-electron integrals $\langle t_{1u}(\pi)x|l_z|t_{1u}(\pi)y\rangle$ and $-{}^1/_2\langle t_{1u}{}^*x|l_z|t_{1u}{}^*y\rangle$ for $t_{1u}(\pi) \rightarrow a_{1g}$ and $e_g \rightarrow t_{1u}{}^*$, respectively. (Note that a_{1g} and e_g orbitals have zero angular momentum and do not contribute.) Since we do not possess good wave functions for $t_{1u}(\pi)$ and $t_{1u}{}^*$, accurate predictions of these expectation values cannot be made. However, if as a crude first approximation we assume $t_{1u}(\pi)$ to be constructed solely from Cl $3p_\pi$ orbitals and $t_{1u}{}^*$ to be an Sb or Sn 5p orbital, we get $\langle t_{1u}(\pi)x|l_z|t_{1u}(\pi)y\rangle = -i/2$ and $-{}^1/_2\langle t_{1u}{}^*x|l_z|t_{1u}{}^*y\rangle = +i/2$. If these wave functions are at all close to the truth, therefore, we predict magnetic moments of opposite sign for $t_{1u}(\pi)^5a_{1g}$ and $e_g{}^3t_{1u}{}^*$ T_{1u} states. In this case the sign of the MCD should enable the two alternatives to be distinguished.

From group theory alone, it follows that for an $A_{1g} \rightarrow T_{1u}$ transition the ratio of the Faraday parameter A to the dipole strength is given by[17] $A/D = -i\langle T_{1u}x|\mu_z|T_{1u}y\rangle$ where $\boldsymbol{\mu} = -\beta(\mathbf{L} + 2\mathbf{S})$ is the magnetic dipole moment operator. If T_{1u} is a pure spin singlet state, $A/D = i\beta\langle {}^1T_{1u}x|L_z|{}^1T_{1u}y\rangle$. Hence, for $t_{1u}(\pi) \rightarrow a_{1g}$ and $e_g \rightarrow t_{1u}{}^*$ we predict $A/D = +\beta/2$ and $-\beta/2$, respectively. A/D is determined from the experimental MCD and absorption spectra by a fitting procedure described previously.[5] For both $SbCl_6{}^-$ and $SnCl_6{}^{2-}$ we obtain $A/D \sim (0.2\text{–}0.7)\beta$. From the sign of the MCD we therefore conclude that the transitions are indeed $t_{1u}(\pi) \rightarrow a_{1g}$ and exclude $e_g \rightarrow t_{1u}{}^*$.

It should be emphasized immediately that these assignments do rest on numerical calculations of orbital angular momentum and for orbitals whose form is not well known. Nevertheless, reliance is placed only on the signs predicted. Hence, if the assumed forms for the molecular orbitals are at all reasonable, the assignments should be valid. Actually, the observed A/D values are in quite good quantitative agreement with those calculated. Only in order of magnitude, however, can this be held to confirm our arguments.

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Acknowledgment.—We wish to acknowledge the assistance of Mr. R. B. Shiflett in measuring the MCD and absorption spectra of $SbCl_6^-$. This work was supported in part by a grant from the National Science Foundation.

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
UNIVERSITY OF HAWAII, HONOLULU, HAWAII 96822

Preparation and Basicity of Sodium Dimethylamidotrihydroborate(III)[1]

BY JOHN W. GILJE AND RICHARD J. RONAN

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Although borane complexes of many nitrogen-containing Lewis bases have received extensive study over the past several decades, the literature contains remarkably few references to borane derivatives of amides. A sparsely characterized dioxanate of $NaH_3BN(CH_3)_2$, formed in the reaction of dimethylamine borane with sodium hydride, has been reported.[2] Shore and Parry[3] and Burg and Schlesinger[4] all have proposed, on the basis of hydrogen evolution, that NaH_2NBH_3 forms by the reaction of ammonia borane with sodium in liquid ammonia. However, neither group actually isolated or characterized a product. In this note we report an investigation of the reaction between dimethylamine borane and sodium, and the characterization and Brønsted–Lowry acid–base chemistry of sodium dimethylamidotrihydroborate(III), $Na(CH_3)_2NBH_3$.

Experimental Section

All manipulations were performed using standard vacuum-line and/or inert-atmosphere techniques. Ir, nmr, and mass spectra were run on Beckman IR-5, Varian A-60 with variable-temperature probe, and Perkin-Elmer Hitachi RMU-6D spectrometers, respectively.

Dimethylamine borane was prepared from the reaction of diborane with dimethylamine by a method analogous to that reported for the preparation of monomethylamine borane[5] except that diethyl ether was substituted for tetrahydrofuran. Diborane was prepared by the method of Weiss and Shapiro.[6] Ammonia and dimethylamine, obtained from Matheson Co., were dried over sodium from which they were distilled immediately before use.

Reaction of Dimethylamine and Sodium.—In a typical reaction 0.161 g (2.73 mmol) of $(CH_3)_2HNBH_3$ and a glass bulb containing about 0.06 g of sodium were placed in a reaction tube, which was then attached to the vacuum line and evacuated. Approximately 10 ml of anhydrous ammonia was distilled into the tube at −196°, the temperature was raised to −40°, and the ball containing the sodium was broken with a magnetic hammer. There was a rapid evolution of noncondensable gas which was periodically withdrawn using a Toepler pump. After 30 min the gas evolution had ceased, the excess sodium was amalgamated with a few drops of mercury, and the remaining traces of noncondensable gas were removed. The total noncondensable gas produced was measured as 1.31 mmol and identified as H_2 by its mass spectrum. In two similar runs 1.06 mmol of $(CH_3)_2HNBH_3$ produced 0.50 mmol of H_2, and 0.53 mmol of $(CH_3)_2HNBH_3$ produced 0.26 mmol of H_2.

The white, hygroscopic solid which remained in the reaction vessel after the solvent ammonia was distilled off analyzed as $Na(CH_3)_2NBH_3$. *Anal.* Calcd for $Na(CH_3)_2NBH_3$: B, 13.4; hydrolytic H, 3.7; equiv wt, 80.8. Found: B, 13.1; hydrolytic H, 3.6; equiv wt, 81.7.

Hydrolysis of $Na(CH_3)_2NBH_3$ with Strong Acid.—About 2 ml of 12 *N* HCl was frozen into a reaction tube containing 0.0125 g (0.155 mmol) of $Na(CH_3)_2NBH_3$. The tube was sealed and warmed to room temperature during which time gas evolution could be observed. After 15 min the contents of the tube were refrozen to −196°, the tube was opened to the vacuum line, and the noncondensable gas was removed. The tube was then heated to 70° for 1 hr during which period no further gas evolution could be detected. The total noncondensable gas obtained was measured as 0.455 mmol and was identified as H_2 as before. No further gaseous products were observed. An nmr spectrum of the solution remaining after hydrolysis indicated the presence of $(CH_3)_2NH_2^+$. $B(OH)_3$ (0.149 mmol) was detected by titration in the presence of mannitol as described elsewhere.[7]

In attempts to hydrolyze $(CH_3)_2NBH_3^-$ completely in neutral or basic solutions very slow hydrogen evolution was observed with complete hydrolysis requiring at least several days.

Titration Experiments.—In order to minimize any decomposition of $(CH_3)_2NBH_3^-$, solutions of $Na(CH_3)_2NBH_3$ were prepared immediately before each titration by adding about 40 ml of cold (0°) CO_2-free water to a weighed sample of $Na(CH_3)_2NBH_3$ contained in a 50-ml volumetric flask which had also been cooled to 0°. The flask was then placed in a constant-temperature bath held at 20 ± 0.50° and allowed to equilibrate for 0.5 hr after which the solution was made to final volume. Typical solutions were in the range of 0.05–0.005 *M*.

Aliquots of these solutions were titrated with 0.0500 *N* HCl. The pH was recorded during these titrations with a Beckman Expandomatic pH meter equipped with a scale expander and Sargent S-30080-15C calomel and S-30050-15C glass electrodes.

Results and Discussion

In anhydrous liquid ammonia at −40° dimethylamine borane reacts rapidly with sodium to form hydrogen and $Na(CH_3)_2NBH_3$ by

$$(CH_3)_2HNBH_3 + Na \longrightarrow 0.5H_2 + Na(CH_3)_2NBH_3$$

Although infrared spectra taken of $Na(CH_3)_2NBH_3$ were always contaminated with $(CH_3)_2HNBH_3$ which formed through the reaction of $(CH_3)_2NBH_3^-$ with trace moisture in the KBr pellets or mulling agents, the strong- and medium-intensity peaks in the spectrum were determined by examination of a number of spectra from which the peaks due to the dimethylamine borane could be removed by inspection. The following bands (in cm^{-1}) were thus obtained: 3080 m, 2920 m, 2330 s, 2240 s, 1440 s, 1155 s, 1136 s, 882 s, 865 m, 694 w. The proton magnetic resonance spectrum of $Na(CH_3)_2NBH_3$ was recorded in liquid ammonia at −35°. The methyl

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