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Paramagnetic Cluster Ions $[\mathrm{B_6Hal}_n\mathrm{Hal'}_{6-n}]^{\bullet-}$ (Hal, Hal′ = Cl, Br, I). EPR Evidence for Radical Stabilization through Electronic Effects of the Halogen Substituents

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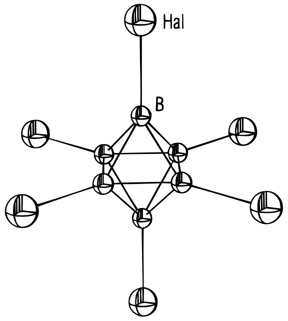
Monoanionic hexaborate cluster radicals $[\mathrm{B_6Hal}_n\mathrm{Hal'}_{6-n}]^{\bullet-}$ with mixed halogen substitution were prepared from oxidizable dianionic precursors and were characterized by vibrational and UV−vis spectroscopy. EPR studies of these and the structurally established homoleptic species $[\mathrm{B_6Hal_6}]^{\bullet-}$ (Hal = Cl, Br, I) reveal strongly increasing g anisotropy and relaxation rate on replacing Cl by Br and especially I substituents; the very stable $\mathrm{B_6I_6}^{\bullet-}$ ion ($g_1 = 2.04$, $g_2 = 1.66$, $g_3 = 1.15$) thus exhibits an EPR spectrum only at 4 K. The extent of these effects is attributed to the Jahn−Teller situation in $[\mathrm{B_6X_6}]^{\bullet-}$ with only partial occupancy of a degenerate MO. Both the absence of B−H bonds and the evidently strong participation of the halogen substituents in the singly occupied MO contribute to the extraordinary stability of these cluster radicals.

In contrast to the large number of persistent carbon-centered radicals in organic, organometallic, and biochemistry there have been few unambiguously identified radicals and radical ions with predominantly boron-centered spin.[1,2] This holds especially for polyborate clusters with their otherwise multi-faceted chemistry and very diverse structures. Reports on $\mathrm{B_8H_8}^{\bullet-}$ [3] and $\mathrm{B_{10}H_{10}}^{\bullet-}$ [4] intermediates have appeared and stable species $\mathrm{B_9Hal_9}^{\bullet-}$ are known;[5] a neutral carborane radical $\mathrm{CB_{11}Me_{12}}^{\bullet}$ was structurally characterized recently.[6]

Whereas the isolability of the latter was attributed to steric protection of the carborane cluster core by a “sheath of methyl groups“,[6] the stability of oxidatively generated and structurally studied cluster anions $[\mathrm{B_6Hal_6}]^{\bullet-}$, Hal = Cl, Br, I,[7] cannot be traced to purely steric effects. These compounds exhibit a close to octahedral hexaborate core and a hexahalogeno substituent sphere.[7]



In this work we describe the synthesis of a number of mixed derivatives $[\mathrm{B_6Hal}_n\mathrm{Hal'}_{6-n}]^{\bullet-}$; we also present their spectroscopic characterization and a first EPR study of these mixed systems and of the homoleptic analogues $[\mathrm{B_6Hal_6}]^{\bullet-}$. The latter are of special interest because, like the calculated parent ion $\mathrm{B_6H_6}^{\bullet-}$,[8] they should have a degenerate doublet ground state in O_h symmetry which may give rise to symmetry reduction and thus Jahn−Teller distortion of the cluster. As a consequence of this situation one can expect close-lying states which, especially in the presence of heavy atoms with large spin−orbit coupling constants, can cause considerable g factor deviation from the free electron value of 2.0023 and severe EPR line broadening due to rapid relaxation,[9] phenomena which are more familiar for paramagnetic transition metal compounds.

Experimental Section

Instrumentation. EPR spectra were recorded in the X band on a Bruker ESP 300 system equipped with a Bruker ER035M gaussmeter and an HP 5350B microwave counter. Spectroelectrochemical measurements were carried out with a two-electrode EPR capillary. Simulations were performed using the program WINEPR SIMFONIA (Bruker). Infrared spectra at 60 K were obtained on a Fourier transform infrared spectrometer NIC-7199 of Nicolet Instruments. Raman spectra were measured at ambient temperature on a Fourier transform Raman spectrometer IFS 66/CS (Bruker). UV−vis spectra were recorded on

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Table 1. Electrochemical Data[a] for the Oxidation of the Dianionic Clusters $[B_6Cl_nHal_{6-n}]^{2-}$ (Hal = Br, I; n = 1, 3, 4, 5) in 10^{-4} M Acetonitrile Solution/0.1 M Bu_4NClO_4

	Hal = Br		Hal = I	
	E_{pa}	E_{pc}	E_{pa}	E_{pc}
$[B_6Cl_6]^{2-}$	0.550	0.608	0.550	0.608
$[B_6Cl_5Hal]^{2-}$	0.616	0.665	0.649	0.723
cis-$[B_6Cl_4Hal_2]^{2-}$	0.642	0.688	0.710	0.745
$[B_6ClHal_5]^{2-}$	0.744	0.813	0.740	0.814
$[B_6Hal_6]^{2-}$	0.739	0.798	0.855	0.913

[a] Peak potentials (in V) vs Ag/AgCl/LiCl in ethanol.

Table 2. Vibrational Data (in cm^{-1}) of the Radical Anions $[B_6Cl_nHal_{6-n}]^{\bullet -}$ (Hal = Br, I; n = 1, 4, 5) in KBr from IR and Raman Spectroscopy

	Hal = Br		Hal = I	
	IR	Raman	IR	Raman
$[B_6Cl_5Hal]^{\bullet -}$	940	258, 325	942	228, 324
trans-$[B_6Cl_4Hal_2]^{\bullet -}$	936	205, 325	943	112, 153, 230, 327
cis-$[B_6Cl_4Hal_2]^{\bullet -}$	936	261, 315	903	112, 153, 228, 323
$[B_6ClHal_5]^{\bullet -}$	918	209, 256	923	148, 221

a Cary 5 spectrophotometer (Varian). Cyclic voltammetric measurements were performed on a Polarecord E626 by Metrohm (Herisau, Switzerland).

Syntheses (General Procedure).[7,10] An ice-cooled solution of 140 mg (0.25 mmol) of $(NH_4)_2Ce(NO_3)_6$ in 5 mL of ethanol was added to an ice-cooled suspension of 0.2 mmol of freshly precipitated $[(n\text{-}C_3H_7)_4N]_2[B_6Cl_nHal_{6-n}]$ [10] (Hal = Br, I; n = 1, 4, 5) in 5 mL of ethanol. After the solution had become clear, it was poured into 200 mL of cold water to precipitate the tetra-*n*-propylammonium salts of the colored radical compounds. The products were separated and washed with water, cold methanol (−25 °C), and diethyl ether. Isolated yields after drying in a vacuum were about 50%. The radical cluster compounds are soluble in alcohols, dichloromethane, and acetonitrile but are insoluble in water and diethyl ether. The solid salts are air-stable but require protection from moisture and light. In dichloromethane solution at 5 °C the half-lives of the homoleptic species $[B_6Hal_6]^{\bullet -}$ (Hal = Cl, Br, I) are 10 h (Hal = Cl), 6 days (Br), and 70 days (I), respectively. At −25 °C the values are 7 days (Cl), 100 days (Br), and >1 year (I).[7b] The half-lives of the heteroleptic species fall in the ranges between the values of the corresponding homoleptic compounds. Spectroscopic data are summarized in Tables 2−4.

Results and Discussion

Electrochemistry. Cyclic voltammetric measurements of ∼10^{-4} M solutions of the heteroleptic cluster dianions $[B_6Cl_nHal_{6-n}]^{2-}$ (Hal = Br, I; n = 1, 4, 5) in acetonitrile/0.1 M Bu_4NClO_4 show that the oxidation reactions yielding the radical anions are reversible, as was formerly observed for the homoleptic analogues.[7,11] Clearly, the redox potentials increase with the number of heavier halogen substituents (Table 1).

Vibrational Spectroscopy. The infrared spectra of the radical ions $[B_6Hal_nHal'_{6-n}]^{\bullet -}$ exhibit weak broad bands in the region of boron cluster vibrations (Table 2). As has been observed earlier for homoleptic perhalogenated species,[7] these bands are shifted by 140−180 cm^{-1} to lower wavenumbers when compared with the dianionic cluster precursors,[11] indicating the weakening of boron−boron bonds on oxidation. In contrast, the Raman-active boron−halogen stretching vibrations are observed at slightly higher frequencies, thus revealing a slight strengthening of the boron−halogen bonds.

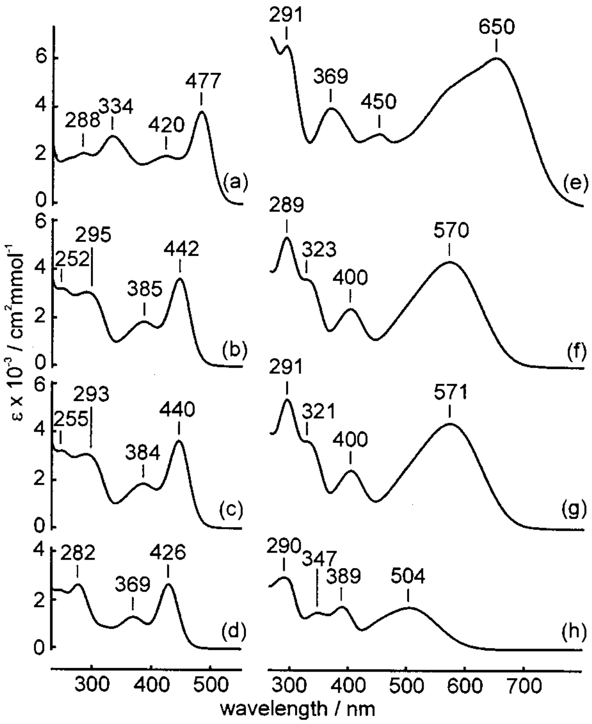

Figure 1. UV−vis spectra of the tetra-*n*-propylammonium salts of $[B_6ClBr_5]^-$ (a), *trans*-$[B_6Cl_4Br_2]^-$ (b), *cis*-$[B_6Cl_4Br_2]^-$ (c), $[B_6Cl_5Br]^-$ (d), $[B_6ClI_5]^-$ (e), *trans*-$[B_6Cl_4I_2]^-$ (f), *cis*-$[B_6Cl_4I_2]^-$ (g), and $[B_6Cl_5I]^-$ (h) in CH_2Cl_2.

UV−Vis Spectra. The UV−vis absorption spectra of the radical ions $[B_6Hal_nHal'_{6-n}]^{\bullet -}$ exhibit characteristic features (Figure 1). Absorption bands above 300 nm are systematically dependent in energy and intensity on the halogenation pattern. Thus, within the Cl/Br and Cl/I series the absorption maxima are shifted bathochromatically and the intensity increases with the number of the heavier halogen atoms. Both effects have been discovered earlier for homoleptic perhalogenated hexaborate radical ions.[7] The pairs of geometrical isomers *cis/trans*-$[B_6Cl_4Br_2]^{\bullet -}$ and *cis/trans*-$[B_6Cl_4I_2]^{\bullet -}$ show very similar absorption spectra. In contrast, absorptions in the high-energy region (λ < 300 nm) show no characteristic dependence on the halogen substitution. On account of these observations we conclude that the low-energy bands represent CT transitions from the halogens to the B_6 cage, while bands below 300 nm are attributed to transitions within the B_6 cage. An exact assignment of transitions in these open-shell systems with heavy atom substituents is not possible at this time.

EPR Spectroscopy. All cluster anions $[B_6Hal_nHal'_{6-n}]^{\bullet -}$ exhibit intense EPR signals in methylene chloride solution, some, however, exhibit signals only at very low temperatures in the frozen state (Figures 2 and 3, Table 3). Increasing substitution with the heavier halogens generally increases the relaxation rate and thus prevents the observation of EPR signals at higher temperatures. Such behavior is known for paramagnetic doublet systems with two or more heavy elements (e.g. Fe, Ru, Os;[12a−c] Ga, In[12d]); organopolyhalogen radicals such as

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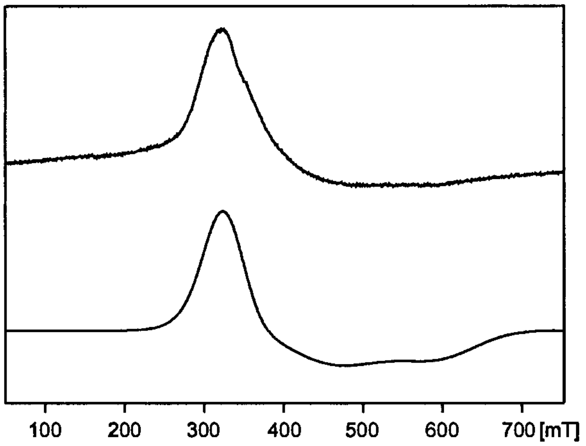

Figure 2. EPR spectrum of $[B_6I_6]^{\bullet-}$ as $(n\text{-Bu})_4N$ salt in dichloromethane at 4 K (top, $\nu = 9.63819$ GHz); computer-simulated spectrum with the parameters from Table 3 (bottom).

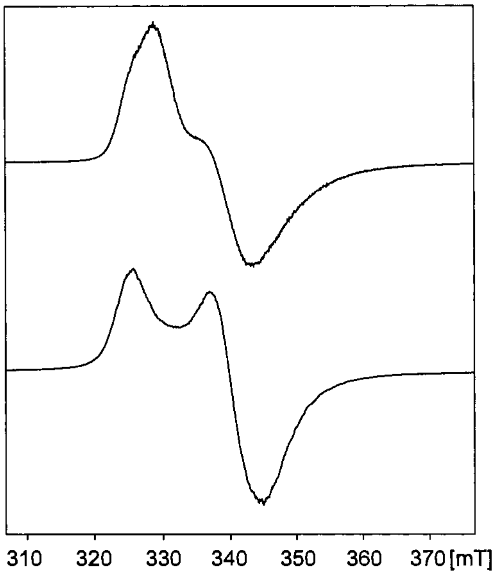

Figure 3. EPR spectra of *cis*-$[B_6Cl_4Br_2]^{\bullet-}$ (top) and *trans*-$[B_6Cl_4Br_2]^{\bullet-}$ (bottom) in dichloromethane at 4 K ($\nu = 9.63885$ GHz).

Table 3. g Factor Data[a] for Perhalogenated Boron Cluster Anions

cluster radical	g_1	g_2	g_3	$\langle g \rangle^b$	$g_1 - g_3$
$[B_6Cl_6]^{\bullet-}$	2.027	2.027	2.027	2.027	0.000
$[^{11}B_6Cl_6]^{\bullet-}$	2.027	2.027	2.027	2.027	0.000
$[B_6Br_6]^{\bullet-\,c}$	2.15	2.09	1.88	2.043	0.27
$[B_6I_6]^{\bullet-\,d}$	2.04	1.66	1.15	1.657	0.89
$[B_6Cl_5Br]^{\bullet-}$	2.041	2.024	2.024	2.030	0.017
$[B_6Cl_5I]^{\bullet-}$	2.055	2.012	2.012	2.026	0.043
trans-$[B_6Cl_4Br_2]^{\bullet-}$	2.117	2.012	2.004	2.045	0.113
cis-$[B_6Cl_4Br_2]^{\bullet-}$	2.101	2.025	2.007	2.044	0.094
trans-$[B_6Cl_4I_2]^{\bullet-}$	2.25	1.99	1.89	2.049	0.36
cis-$[B_6Cl_4I_2]^{\bullet-}$	2.145	2.051	2.022	2.073	0.123
$[B_6ClBr_5]^{\bullet-}$	2.137	2.041	1.943	2.041	0.194
$[B_6ClI_5]^{\bullet-}$	2.206	1.730	1.265	1.832	0.94

[a] From simulation of X band EPR spectra of frozen solutions at 4 K in dichloromethane. [b] Calculated from $\langle g \rangle = [{}^1/_3(g_1{}^2 + g_2{}^2 + g_3{}^2)]^{1/2}$. [c] Not observable at 300 K. [d] Not observable at 77 K.

the tetrahalogenosemiquinones do not exhibit such effects.[13] Rapid relaxation typically occurs from close-lying excited states to the doublet ground state, especially in the presence of strongly contributing atoms with high spin–orbit coupling constants.[14]

Hyperfine interaction was not observed for the systems studied here, although all participating atoms consist of isotopes with nonzero nuclear spin. Hyperfine coupling of more than one boron center with the natural isotopic composition ^{10}B ($I = 3$, 19.8% nuclear abundance) and ^{11}B ($I = {}^3/_2$, 80.2%) generally leads to complicated patterns[1,2,15] and may eventually result in the total absence of resolution due to numerous overlapping lines. (Assuming octahedral symmetry and neglecting configurational isomerism, there are seven isotope combinations $(^{10}B)_n(^{11}B)_{6-n}$ with no less than 19 theoretical lines per combination). The number of six equivalent boron centers and the relatively small isotropic hyperfine constants a_o[14] of ^{10}B ($a_o = 30.43$ mT) and ^{11}B ($a_o = 90.88$ mT) suggests relatively small coupling from the boron nuclei. This suggestion is supported by a study of the $[^{11}B_6Cl_6]^{\bullet-}$ cluster (99.5% ^{11}B). There is no discernible difference in the EPR signals (including line width) of this species and the cluster with boron nuclei in natural isotopic abundance (Table 3).

The halogen atoms, on the other hand, which participate to a considerable extent in the spin distribution, as is evident from the g component behavior (cf. below), have similarly unfavorable properties for the resolution of EPR hyperfine structure. The light chlorine isotopes ^{35}Cl ($I = {}^3/_2$, 75.77%) and ^{37}Cl ($I = {}^3/_2$, 24.23%) have rather small isotropic hyperfine constants a_o of 204.21 and 169.98 mT, respectively. The a_o values of the isotopes ^{79}Br ($I = {}^3/_2$, 50.69%) and ^{81}Br ($I = {}^3/_2$, 49.31%) are larger (1144.34 and 1233.52 mT); however, the EPR line width increases considerably when lighter elements are substituted by heavier homologues.[16] This effect becomes even more dominant for the iodo-substituted species; despite the large a_o value of 1484.40 mT for ^{127}I ($I = {}^5/_2$, 100%) and obvious participation of the halogens in the singly occupied MO (SOMO), there is no hyperfine splitting observable for species such as $B_6I_6{}^{\bullet-}$ or $BCl_5I^{\bullet-}$.

In the absence of hyperfine information we can use the g factor components as source to study the electronic structures of the species $[B_6Hal_nHal'_{6-n}]^{\bullet-}$. In frozen dichloromethane solution the cluster anions exhibit a g component anisotropy $g_1 - g_3$ which clearly increases with the number of heavier halogen substituents. The reason is the dependence[14] of $g - g_{\text{electron}}$, the g factor deviation from the free electron value of $g = 2.0023$, on the spin–orbit coupling constant ξ

$$g = g_e - \frac{2}{3}\sum_i \sum_n \sum_{k,j} \frac{\langle \psi_0 | \xi_k \mathbf{L}_{ik} \delta_k | \psi_n \rangle \langle \psi_n | \mathbf{L}_{ij} \delta_j | \psi_0 \rangle}{E_n - E_0} \qquad (1)$$

where $g_e = 2.0023$, E_0 is the energy of singly occupied molecular orbital, E_n are the energies of empty or doubly occupied MOs, ξ_k is the spin-orbit coupling constant, and $\mathbf{L}$ = angular momentum operator.

The value of ξ shows a strong increase on going from Cl (approximately 700 cm^{-1}) via Br (2460 cm^{-1}) to I (5060 cm^{-1}),[13] which results in particularly strong g factor deviations for the periodo species.[5,13]

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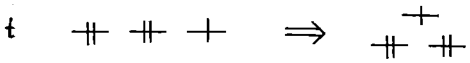
The “symmetry“ of the *g* factor splitting is quite informative: Whereas no *g* anisotropy could be observed for the $B_6Cl_6^{\bullet -}$ species due to the line width and contributions of just the light boron and chlorine atoms, most other species exhibit three *g* components in the frozen state. This result, even for the $B_6Br_6^{\bullet -}$ and $B_6I_6^{\bullet -}$ species, suggests a low-symmetry situation for the unpaired electron and probably a distorted structure. Crystal structure analyses have shown strongly distorted[7a] or close to octahedral[7b] cluster arrangenments, depending on the counterion (e.g. for $B_6I_6^{\bullet -}$). We thus assume considerable structural flexibility and a propensity for cluster distortion as supported by the Jahn−Teller situation (degenerate t orbitals[8]).

Those mixed halide species which have one heavy halide Hal different from five light chloride substituents display axial *g* factor splitting, probably due to the dominant effect of the B−Hal molecular axis. Similarly, of the *cis/trans*-$[B_6Cl_4Br_2]^{\bullet -}$ isomers, the trans species exhibits a distinctly less rhombic splitting of *g* components ($g_1 - g_2 = 0.105$, $g_2 - g_3 = 0.008$) than the cis isomer ($g_1 - g_2 = 0.076$, $g_2 - g_3 = 0.018$; Figure 3 and Table 3). In the *cis/trans*-$[B_6Cl_4I_2]^{\bullet -}$ isomer series the main difference is the much larger *g* anisotropy of the trans species relative to the cis isomer.

The dependence of the individual *g* components and of the calculated average $\langle g \rangle$ values (Table 3) merits special inspection. By applying[9] the above equation, the deviation of $\langle g \rangle$ to higher values than 2 (as observed for most chloride-rich species) can be understood as a consequence[9,14] of the Jahn−Teller situation where *fully occupied* orbitals lie close to the SOMO (Chart 1).

Chart 1



A deviation of $\langle g \rangle$ to values lower than 2 occurs only for $B_6I_6^{\bullet -}$ and $B_6I_5Cl^{\bullet -}$, i.e., for iodine-rich species. One *g* component in particular is lowered in these systems to very low values which suggests[14] the presence of excited states with nonzero angular orbital momentum lying close to the doublet ground state of the paramagnetic cluster anion. These states could tentatively be associated with combinations of *unoccupied* σ*(B−I) orbitals which are also held responsible for the rapid relaxation; no corresponding *g* factor and relaxation effects were observed for $B_9Hal_9^{\bullet -}$ species, e.g. for $B_9I_9^{\bullet -}$ with $g_1 = 2.37$, $g_2 = 2.125$, and $g_3 = 2.095$,[5b] where the singly occupied MO is nondegenerate.[5b,17] We thus conclude that the perhalogeno substitution stabilizes the $[B_6Hal_6]^{\bullet -}$ ions not only through some steric protection and the reluctance to form Hal^+ as a leaving group on oxidation, there also seems to be a positive stabilizing effect from the electronic interaction between the B_6 core and the hexahalogen shell. Unfortunately, calculations of excited states or *g* factors of these open-shell systems with less-defined structure and several heavy elements with appreciable spin−orbit coupling constants are currently beyond our capabilities.

In summary, the unusually persistent radical cluster anions $[B_6Hal_nHal'_{6-n}]^{\bullet -}$ exhibit remarkable EPR spectroscopic features which suggest strong participation of the halogen substituents in the singly occupied MO. In agreement with the EPR results, the iodo-substituted systems display the highest stability, suggesting that the halogens are essential for the persistence of these clusters.

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