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Electron Spin Resonance Spectra and Spin-Hamiltonian Parameters for Trigonal-Bipyramidal Nickel(I) and Copper(II) Complexes

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The ESR spectra of five-coordinate trigonal-bipyramidal copper(II) complexes have been far less investigated than those of complexes which can be considered as derived from octahedral or tetrahedral stereochemistries.[2] The data for other d^9 ions are still scarcer. In particular no ESR data have been reported up to now in the literature for trigonal-bipyramidal nickel(I) complexes, although several well-documented and relatively stable compounds of this kind have been recently synthesized and characterized.[3,4] In all reported cases of trigonal-bipyramidal copper(II) complexes[5–7] the observed pattern exhibited $g_{\|} = 2.0023 = g_e < g_{\perp}$ suggesting that the unpaired electron had to be placed in an orbital which was mainly metal d_{z^2}. However both positive and negative deviations of $g_{\|}$ from g_e were observed. In particular $g_{\|}$ values sensibly lower than g_e were observed in the frozen-solution spectra of $[CuX(Me_6tren)]^+$ (where Me_6tren is tris(2-dimethylaminoethyl)amine and X = Br, I),[7] with higher deviations for the iodide as compared to the bromide derivative. On the other hand $g_{\|}$ values slightly higher than g_e were reported for some complexes[5,6] in which all donor atoms had low spin–orbit coupling constants.

Some explanations were put forward for interpreting this behavior, but since these were based on solution spectra,[7] the nature of low-symmetry components of the ligand field could not be assessed. In order to eliminate these inconveniences we resolved to study the single-crystal ESR spectra of chromophores possessing as high symmetry as possible, however not less than C_3. The only suitable examples of copper(II) complexes, to the best of our knowledge, are $CuX(Me_6tren)X$ and $Cu(NH_3)_2Ag(SCN)_3$ whose x-ray structures have been reported[8,9] and the copper atoms have been found to possess C_3 and D_3 site symmetry, respectively. We wish to report now the ESR spectra of $CuX(Me_6tren)X$ doped into the isomorphous zinc salts and the variable-temperature spectra of $Cu(NH_3)_2Ag(SCN)_3$. Further, unpublished work of our laboratory[10] has shown that the d^9 ion nickel(I) has C_3 site symmetry in the trigonal-bipyramidal complexes $NiX(np_3)$ (X = Cl, Br, I; np_3 = tris(2-diphenylphosphinoethyl)amine) and we wish to report here their powder ESR spectra.

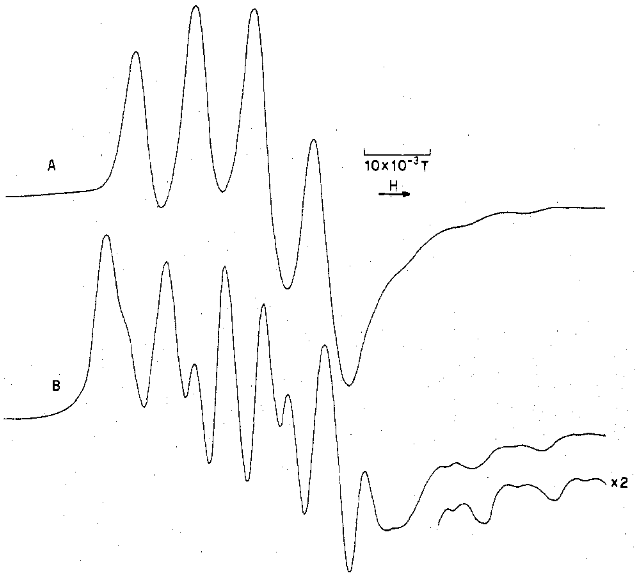

Figure 1. Polycrystalline powder ESR spectra of the $CuX(Me_6tren)X$ complexes doped into the zinc isomorphous salts: A, X = Br; B, X = I.

Table I. Spin-Hamiltonian Parameters for Trigonal-Bipyramidal Copper(II) and Nickel(I) Complexes

	$g_{\|}{}^b$	$g_{\perp}{}^b$	$A_{\|}{}^{a,b}$	$A_{\perp}{}^{a,b}$
$CuBr(Me_6tren)Br$	1.956 (1)	2.182 (1)	+80 (5)	−100 (5)
$CuI(Me_6tren)I$				
Site 1	1.895 (1)	2.226 (1)	+97 (5)	−103 (5)
Site 2	1.922 (1)	2.189 (1)	+99 (5)	−107 (5)
$Cu(NH_3)_2Ag(SCN)_3$				
296 K	2.006 (1)	2.201 (2)		
233 K	2.004 (1)	2.201 (2)		
183 K	2.002 (1)	2.201 (2)		
133 K	2.001 (1)	2.201 (2)		
4.2 K	1.998 (1)	2.199 (2)		
$NiCl(np_3)$	2.001 (1)	2.210 (4)		
$NiBr(np_3)$	2.004 (4)	2.184 (4)		
$NiI(np_3)$	2.004 (4)	2.151 (4)		

[a] All hyperfine coupling constants in units 10^{-4} cm^{-1}. [b] The values in parentheses are the estimated errors.

Experimental Section

All of the compounds were prepared as previously described.[4,11,12] $Cu(NH_3)Ag(SCN)_3$ and $NiX(np_3)$ were used undiluted, since attempts to prepare suitable diamagnetic hosts were unsuccessful. For the Me_6tren complexes about 1% copper-doped powders of the zinc complexes were obtained by slow evaporation of 1-butanol solutions. Powder and single-crystal spectra were recorded with a Varian E-9 spectrometer equipped with X band; variable-temperature spectra were recorded using an Oxford Instruments continuous-flow liquid helium cryostat and a Varian variable-temperature assembly.

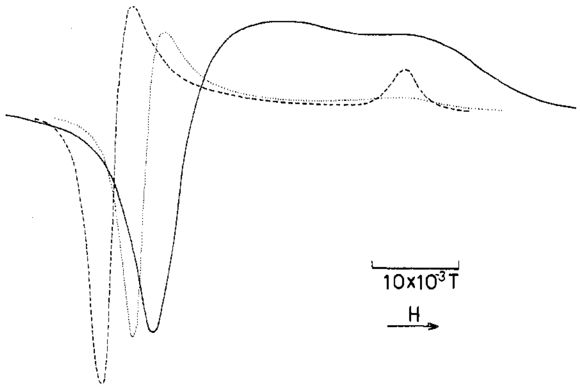

Figure 2. Polycrystalline powder ESR spectra of the NiX(np_3) complexes: ---, X = Cl; ····, X = Br; —, X = I.

Results

The powder spectra of the $[CuX(Me_6tren)]^+$ ion are shown in Figure 1. The spectrum of the bromide derivative shows the usual pattern of trigonal-bipyramidal complexes,[5-7] with the g and A values reported in Table I. The $g_\parallel$ value was checked also by single-crystal spectra, recorded with the static magnetic field parallel to the C_3 crystal axis. The spectra of the iodide derivative show the presence of two different sites, possessing slightly different spin-Hamiltonian parameters, their values being reported in Table I. The observation of different sites in doped crystals which are expected to allow only a single site is not new and has been recently reported for cobalt(II) complexes.[13] It is interesting to note that also in the frozen-solution spectra a doubling of the peaks was observed in the $g_\perp$ region, and it was interpreted as due to rhombic distortions of the chromophore.[7]

The powder spectra of NiX(np_3) are shown in Figure 2. The pattern of the values is the same as in the spectra of the copper(II) complexes. The bandwidth in the $g_\parallel$ region increases on passing from chlorine to iodine, making the $g_\parallel$ value less certain. Unfortunately it was not possible to grow single crystals suitable for ESR analysis.

In order to determine with as much accuracy as possible the $g_\parallel$ values of $Cu(NH_3)Ag(SCN)_3$ single-crystal spectra were recorded at variable temperatures, in the range 4.2–296 K, with the static magnetic field parallel to the C_3 crystal axis and perpendicular to it. The values are reported in Table I. These values were calculated using DPPH ($g = 2.0037 \pm 0.0001$[14]) as a standard. The orientation of the crystals in the magnetic field was accurately checked in order to be sure that the deviation of $g_\parallel$ from g_e was not due to slight misalignments. The peak-to-peak width of the band was temperature dependent, ranging from $5.2 \times 10^{-3}T$ at room temperature to $0.7 \times 10^{-3}T$ at 4.2 K. The estimated error in determining the peak of the resonance absorption was $0.2 \times 10^{-3}T$, yielding the uncertainty in the g values reported in Table I.

Discussion

The results of the previous section show (i) that the previous observations of $g_\parallel$ values different from g_e were correct and that the deviations are not attributable to low-symmetry components of the ligand field and (ii) a theoretical analysis of the spin-Hamiltonian parameters for trigonal-bipyramidal d^9 complexes must justify both positive and negative deviations of $g_\parallel$ from g_e.

The theoretical treatment must be as complete as possible, since group theoretical considerations show that the simple formula for the g values in the MO formalism[15]

$$g_\parallel = g_e + g_e \sum_{m \neq n} \sum_{k,k'} \frac{\langle X_n^{k} | \xi_k(r^k) L_z^{k} | X_m^{k} \rangle \langle X_m^{k'} | L_z^{k'} | X_n^{k'} \rangle}{\epsilon_n - \epsilon_m}$$

does not allow a variation of $g_\parallel$ from g_e. On the other hand full-matrix crystal field spin–orbit coupling calculations, i.e., including corrections of the second order in ζ/Δ, neglected by the above formula, were performed using the reported matrices[16] and the calculated $g_\parallel$ values were in no case lower than perhaps 1.998.

Our choice was therefore to use an MO scheme, labeling the functions according to the C_3 symmetry of the complexes with the tripod ligands. The zero-order functions for the antibonding orbitals which are mainly metal in character are shown in the Appendix, together with some details of the method used to calculate the spin-Hamiltonian parameters. The formulas obtained are

$$g_\parallel = g_e - (2g_e f_1^2/N^2) - (2g_e f_2^2/N^2) - (4/N^2)(f_1c_1 + f_2b_1)^2 + (2/N^2)(f_1c_2 + f_2b_2)^2 + \text{smaller terms} \quad (1)$$

$$g_\perp = (1/N^2)(g_e + 2(6^{1/2}) f_1a_1c_2 + 2(6^{1/2}) f_2a_1b_2 + \text{smaller terms}) \quad (2)$$

$$A_\parallel = (P/N^2)(-\kappa a_1^2 + {}^4/_7 a_1^2 - {}^1/_7 (g_\perp - g_e)) \quad (3)$$

$$A_\perp = (P/N^2)(-\kappa a_1^2 - {}^2/_7 a_1^2 + {}^{15}/_{14} (g_\perp - g_e)) \quad (4)$$

In the limit of D_{3h} symmetry, setting $c_1 = c_3 = b_2 = b_3 = 0$, the preceding expressions reduce to those previously reported, except for terms proportional to $(\zeta/\Delta)^2$. It is easy to recognize that now g_e is an upper limit for $g_\parallel$. The inclusion of the spin-orbit coupling constant of the halogen makes f_1 and f_2 larger than in the case of the pure crystal field approximation, determining a larger reduction of $g_\parallel$ below g_e. Further it can be noted that in the limit of D_{3h} symmetry the contribution corresponding to ζ^X reduces to zero. Finally the effect of the inclusion of ζ^X is also to increase the value of $g_\perp$ (and consequently to make $A_\parallel$ more negative and $A_\perp$ more positive).

It is now apparent that the low $g_\parallel$ values of the CuX(Me_6tren)X complexes can be justified by the contributions from the spin–orbit coupling constant of the halogen. Also the increase of the value on passing from bromine to iodine conforms to this view. Unfortunately the number of parameters required by eq 1–4 is far too large to allow a meaningful fit of the experimental spin-Hamiltonian parameters. However sample calculations using "reasonable" values of the a, b, and c parameters together with the experimental values of the electronic energy separations show that the corrections to the $g_\parallel$ values are of the correct order of magnitude. For instance by using $a_1 = 0.9$, $a_2 = 0.4$, $c_1 = 0.5$, $c_2 = 0.8$, $c_3 = 0.4$, $b_1 = 0.85$, $b_2 = 0.3$, $b_3 = 0.25$, $\zeta^{Br} = -2460$, $\zeta^{I} = -5000$, and $\zeta^{Cu} = -829$ cm^{-1} the values of 1.959 for the bromide and of 1.923 for the iodide derivative are obtained using $\Delta_1 = 13\,200$, $\Delta_2 = 10\,300$ cm^{-1} for the former and $\Delta_1 = 12\,900$, $\Delta_2 = 9900$ cm^{-1} for the latter.[17]

In the case of the NiX(np_3) complexes it seems that the effect of the spin–orbit coupling constant of the halogen is not so marked, since (i) the $g_\parallel$ values are in every case quite close to g_e and (ii) no appreciable lowering of $g_\parallel$ is observed on passing from chlorine to iodine. Further, in this case the $g_\perp$ values follow the reverse pattern as compared to the CuX(Me_6tren)X complexes, decreasing in the order Cl > Br > I, and this is precisely the order to be expected by considering the different nephelauxetic behavior of the halogens and neglecting the contribution from their spin–orbit coupling constant.

The other main problem seen in the ESR spectra of trigonal-bipyramidal copper(II) complexes is that of explaining $g_\parallel$ values greater than g_e. As a matter of fact the $g_\parallel$ value of $Cu(NH_3)_2Ag(SCN)_3$ at room temperature is 2.006, but it is reduced to 1.998 at 4.2 K. Equation 1 can by no means justify such behavior. A positive deviation from g_e might be brought about only by terms linear in (ζ/Δ), but these are zero by symmetry, since as long as the C_3 axis is preserved, no function having orbital contribution can be admixed into the ground state.

A possible mechanism altering the D_3 site symmetry might be the free rotation of the axial ammonia molecules, but this cannot destroy the trigonal symmetry. Further in this scheme one would expect a higher symmetry at high temperature, as observed in nickel–ammonia complexes,[18] predicting a temperature dependence opposite to that observed.

Another possible mechanism is the vibronic coupling,[19] which, by lowering the instantaneous symmetry of the complex, allows the admixing of excited E levels into the ground state. In D_{3h} symmetry an E′ vibration can admix ^{2}E′ levels into the $^2A_2'$ ground level. By using a crystal field formalism and the Hamiltonian described in the Appendix by means of standard techniques it can be shown that

$$g_{\parallel} = g_e - 8\beta^2\zeta/(N^2(1+\beta^2)\Delta_2) + \text{smaller terms} \qquad (5)$$

$$g_{\perp} = (1/N^2(1+\beta^2))(g_e - 6\zeta/\Delta_1 - 2\beta^2\zeta/\Delta_1) + \text{smaller terms} \qquad (6)$$

The terms $(1+\beta^2)$ and N^2 derive from the normalization conditions of the ground state respectively before and after the application of spin–orbit coupling as a perturbation. Since β^2 depends on vibronic mixing, it is expected to decrease as the temperature is lowered.[20] As a consequence $g_{\parallel}$ is expected to decrease on cooling, while $g_{\perp}$ is expected to increase. Further the variation has to be more marked for $g_{\parallel}$, while it has to be very small for $g_{\perp}$. The values of Table I show that $g_{\parallel}$ decreases with temperature beyond experimental error and the 4.2-K value can be calculated with crystal field methods, as would be expected on the basis of the nature of the donor atoms. The room-temperature and 4.2-K values of $g_{\perp}$ are not different within experimental error. Sample calculations using (5) and (6) and the values $\beta^2 = 0.01$, $\zeta^{Cu} = -380$ cm^{-1}, $\Delta_1 = 11\,300$, and $\Delta_2 = 10\,500$ cm^{-1} yield $\Delta g_{\parallel} = 0.003$ and $\Delta g_{\perp} = 0.203$. Repeating the same calculation with $\beta^2 = 0$ one gets $\Delta g_{\parallel} = 0$ and $\Delta g_{\perp} = 0.204$. Therefore it seems that the vibronic mechanism can reproduce, in principle, the observed behavior with temperature of $g_{\parallel}$. For $g_{\perp}$ the predicted increase with decreasing temperature is not observed, but the value is substantially constant. However the small variation expected may be masked by the experimental error.

These results show once more how the possibility of extracting MO coefficients from experimental spin-Hamiltonian parameters is very questionable, since sizable experimental effects can be justified only including "small" terms, which in turn introduce a far too large number of parameters. However the use of strictly symmetric chromophores allowed us to give at least a semiquantitative explanation of the observed spin-Hamiltonian parameters and showed how vibronic coupling, which is well known to influence the electronic spectra, can produce measurable effects also on the ESR spectra in cases where any Jahn–Teller effect is out of the question.

Appendix A

Spin-Hamiltonian Parameters for MXLL′$_3$ Chromophores. The zero-order functions for the antibonding orbitals which are mainly metal 3d in character are reported in Table II. The unpaired electron has to be placed in the $|A_1\rangle$ orbital, which under spin–orbit coupling can be admixed with excited E states[22] yielding to first order

$$|a_1\pm\rangle = \frac{1}{N}[|A_1\pm\rangle + f_1|E(1),\pm1\mp\rangle + f_2|E(2),\pm1\mp\rangle]$$

Table II. Antibonding Orbitals for a d^1 Ion in C_{3v} Symmetry[a]

$|A_1\rangle = a_1|0,M\rangle - a_2|0,X\rangle - a_3|0,L_{ax}\rangle - a_4|A_1,L_{eq}\rangle$

$|E(1),1\rangle = c_1|-2,M\rangle + c_2|1,M\rangle - c_3|1,X\rangle - c_4|1,L_{ax}\rangle - c_5|E(1),1,L_{eq}\rangle$

$|E(1),-1\rangle = c_1|2,M\rangle + c_2|-1,M\rangle - c_3|-1,X\rangle - c_4|-1,L_{ax}\rangle - c_5|E(1),-1,L_{eq}\rangle$

$|E(2),1\rangle = b_1|-2,M\rangle + b_2|1,M\rangle - b_3|1,X\rangle - b_4|1,L_{ax}\rangle - b_5|E(2),1,L_{eq}\rangle$

$|E(2),-1\rangle = b_1|2,M\rangle + b_2|-1,M\rangle - b_3|-1,X\rangle - b_4|-1,L_{ax}\rangle - b_5|E(2),-1,L_{eq}\rangle$

[a] The labels (1) and (2) identify the two E species of C_{3v} symmetry. 1 and −1 identify their components. All the *a, b, c* coefficients must be taken as positive quantities.

with

$$N^2 = 1 + f_1^2 + f_2^2$$

$$f_1 = -\frac{\langle E(1),\pm1\mp|\mathcal{H}_{so}|A_1\pm\rangle}{\Delta_1} = -\frac{1}{\Delta_1}\left[\frac{6^{1/2}}{2}c_2a_1\zeta_d{}^M + \frac{2^{1/2}}{2}c_3a_2\zeta_p{}^X\right]$$

$$f_2 = -\frac{\langle E(2),\pm1\mp|\mathcal{H}_{so}|A_1\pm\rangle}{\Delta_2} = -\frac{1}{\Delta_2}\left[\frac{6^{1/2}}{2}b_2a_1\zeta_d{}^M + \frac{2^{1/2}}{2}b_3a_2\zeta_p{}^X\right]$$

$\mathcal{H}$so is the spin–orbit coupling Hamiltonian

$$\mathcal{H}_{so} = [\xi^M(r_M)]\mathbf{l}_M\cdot s + \sum_{L,L',X}[\xi^L(r_L)]\mathbf{l}_L\cdot s$$

where $\mathbf{l}_M$ and $\mathbf{l}_L$ are the angular momentum operators centered on the metal and ligand nucleus. $\zeta_d{}^M$ and $\zeta_p{}^X$ are the spin–orbit coupling constants of the metal and halogen atoms and Δ_1 and Δ_2 represent the energy separations between the ground state and the E(1) and E(2) excited ones.

In deriving these expressions we have neglected multiple-center integrals like $\langle\Gamma,X|\xi^M(r_M)|0,M\rangle$ and $\langle\Gamma,M|\xi^L(r_L)|0,X\rangle$ where Γ refers to the functions reported in Table II, because of the r^{-3} dependence of $\xi(r)$, and terms containing ζ^L and $\zeta^{L'}$ have not been considered owing to the small value of the spin–orbit coupling constants of L and L′ as compared to the metal and halogen ones. With these basis functions, using standard methods of calculations[23] and neglecting terms containing the overlap integrals and the *c* and *b* coefficients of L and L′, we have obtained the expressions 1–4 for the **g** and **A** tensors.

Effect of the Vibronic Coupling on the *g* Values for the Chromophore Cu(NH$_3$)$_2$(SCN)$_3$. In D_{3h} symmetry an E′ vibration can admix ^{2}E′ excited states into the $^2A_2'$ ground state. If, for the sake of simplicity, we use a crystal field formalism, the functions $|xy\rangle$ and $|x^2-y^2\rangle$ span the ^{2}E′ irreducible representation and $|z^2\rangle$ spans the $^2A_2'$ one. The appropriate Hamiltonian describing the vibronic mixing[21] takes the form

$$\mathcal{H}_v = q_{xy}Q_{xy} + q_{x^2-y^2}Q_{x^2-y^2}$$

Here the subscripts xy and x^2-y^2 mean that the function spans the same irreducible representation of the D_{3h} group as $|xy\rangle$ and $|x^2-y^2\rangle$ do.

The ground-state function corrected to first order in perturbation calculation is

$$|f\rangle = \frac{1}{(1+\beta^2)^{1/2}}\left[|z^2\rangle + \frac{\beta}{2}(|xy\rangle + |x^2-y^2\rangle)\right]$$

where β, the coefficient of vibronic mixing, assuming for simplicity that no quanta of vibration are present in the fundamental state, takes the form

$$\beta = \left(\frac{\hbar}{2\nu}\right)^{1/2} \frac{\langle xy | q_{xy} | z^2 \rangle}{\Delta_2} = \left(\frac{\hbar}{2\nu}\right)^{1/2} \frac{\langle x^2 - y^2 | q_{x^2-y^2} | z^2 \rangle}{\Delta_2}$$

In this expression Δ_2 is the energy difference between $^2A_2'$ and $^2E'$. Expressions 5 and 6 for $g_\parallel$ and $g_\perp$ have been obtained by means of standard methods of calculation,[23] neglecting terms in ζ^2/Δ_2^2 and β^2.

Registry No. CuBr(Me$_6$tren)Br, 14405-54-0; CuI(Me$_6$tren)I, 59172-14-4; Cu(NH$_3$)$_2$Ag(SCN)$_3$, 12075-57-9; NiCl(np$_3$), 54423-06-2; NiBr(np$_3$), 54382-82-0; NiI(np$_3$), 54353-75-2.

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Synthesis of μ-Disulfido-bis(undecahydro-*closo*-dodecaborate)(4−) and of a Derived Free Radical

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We report the isolation and some properties of tetracesium μ-disulfido-bis(undecahydro-*closo*-dodecaborate)(4−) hemihydrate, $Cs_4B_{12}H_{11}SSB_{12}H_{11}\cdot 0.5H_2O$, following the oxidation of $B_{12}H_{11}SH^{2-}$ with iodosobenzoate.

$B_{12}H_{11}SSB_{12}H_{11}^{4-}$ is of particular interest in the neutron-capture therapy of gliomas[2a] as it may possess favorable biological properties.[2b,3]

Prior to the synthesis of this compound, the oxidative coupling of two polyhedral borane anions has been accomplished chemically only for $B_{10}H_{10}^{2-}$ and $B_{10}H_9(\text{ligand})^-$.[4] Oxidation of $B_{10}H_{10}^{2-}$ with Fe(III) or Ce(IV) in aqueous solution produces $B_{20}H_{18}^{2-}$ in which the two B_{10} polyhedra are connected by three center B–B–B bonds.[5,6] Subsequent reduction of $B_{20}H_{18}^{2-}$ yields $B_{20}H_{18}^{4-}$ in which a single B–B bond links both cages.[6,7] Another type of bond linking two B_{10} polyhedra is produced by the ultraviolet irradiation of $B_{20}H_{18}^{2-}$.[8] This product, an isomer of $B_{20}H_{18}^{2-}$, has two B–H–B three-center bonds joining the cages. Oxidation of $B_{10}H_{10}^{2-}$ may also be accomplished by NO_2 to produce $B_{20}H_{18}NO^{3-}$,[9,10] in which a bridging NO group links the cages. The $B_{12}H_{12}^{2-}$ anion and several polyhedral heteroborane anions have also been coupled, though only via electrochemical oxidation.[11,12]

Although the product described here, $B_{12}H_{11}SSB_{12}H_{11}^{4-}$, is the first example of two borane anions being linked by a disulfide bridge, several other disulfides are known in polyhedral borane chemistry and include the neutral disulfides of mercapto-*o*-carboranes, $RCB_{10}H_{10}CSH$, and the disulfide of the metallocarborane $(1,2\text{-}B_9C_2H_{10})Co(SH)_2^-$.[13,14] The latter disulfide is interesting in that two carbollide ligands are linked via a disulfide bond. The disulfide described in this report is, however, distinguished by its large negative charge, a probable reflection of which is the formation of an exceptionally stable free radical. Some properties of this free radical are also described.

Experimental Section

Spectra. ^{11}B NMR were obtained at 32.1 MHz using a Varian XL-100 with Fourier transform and a pulsed deuterium lock. Samples of the sodium salts, obtained by ion exchange of the cesium salts using Bio-Rad AG 50W-X8 Na$^+$ resin, were dissolved in a 50% solution of D_2O in water to give a final concentration of approximately 0.1 M. The samples were run in 12-mm tubes and referenced relative to external $Et_2O\cdot BF_3$ by sample interchange. Both normal and hydrogen-decoupled spectra were taken and each of these was run with and without line-narrowing techniques.[15] From the latter the ^{11}B chemical shifts and hydrogen coupling constants were obtained. Chemical shifts are estimated to be to an accuracy of ±0.1 ppm and coupling constants to ±6 Hz.

ESR spectra were obtained using an Alfa Scientific Laboratories Al-X-10 spectrometer operating at 9.26 GHz. Field strength was determined by reference to perylene in 98% sulfuric acid. Raman spectra were determined using a Spex Ramalog instrument with a Coherent Radiation Model 52 G argon ion laser (4880-Å excitation). The sample was run as a solid using techniques described elsewhere.[16] Infrared spectra were recorded on a Perkin-Elmer 137 spectrophotometer using KBr pellets. Absorbances in the visible region were observed using a Cary Model 14 spectrophotometer to determine λ_{max}.

Chromatography. Thin-layer chromatography (TLC) was carried out as described elsewhere using Baker-Flex DEAE cellulose thin-layer chromatography sheets.[17] A solvent system of 1:1 v/v 3 M NH_4NO_3–CH_3CN was employed. Visualization was achieved using both palladium chloride and sodium nitroprusside. For the latter technique the TLC sheets, after development, were dipped into a 10% aqueous sodium nitroprusside solution. After excess solution was drained off, the sheets were placed in a jar containing filter paper saturated with concentrated ammonium hydroxide. Under these conditions thiol-containing components visualized as pink spots.

Materials. *o*-Iodosobenzoic acid obtained from K & K Laboratories, Inc., was dissolved in a minimum of aqueous sodium hydroxide and diluted to give a 0.1 M solution at pH 9.5. Trifluoroacetic acid and dithiothreitol were from Aldrich. *N*,*N*-Dimethylformamide, 99 mol % pure from Fisher, was used without further purification. All other solvents were of reagent grade.

Synthesis of $Cs_4B_{12}H_{11}SSB_{12}H_{11}\cdot 0.5H_2O$. To 2.29 g (5 mmol) of $Cs_2B_{12}H_{11}SH\cdot H_2O$[18] in 30 mL of water was slowly added 25 mL of 0.1 M aqueous sodium iodosobenzoate at pH 9.5. A white precipitate formed immediately. Water was evaporated to give a final volume of approximately 10 mL; the flask was cooled in ice and the mixture filtered to yield 1.90 g of product. This salt was dissolved in 100 mL