Table I. Carboranes Formed in the Gas-Phase Pyrolysis of $2\text{-}B_5CH_9$

	R_f[a]	Yield	
		mmol	%[b]
$1,7\text{-}B_6C_2H_8$	2.3	0.033	5
$1,6\text{-}B_8C_2H_{10}$	5.1	Trace	1
$1,7\text{-}B_{10}C_2H_{12}$	13.4	0.105	16
$1,3\text{-}B_7C_2H_{13}$	14.0	0.196	30

[a] Relative to *n*-pentane = 1.00. [b] Based on conversion of 2 mol of $2\text{-}B_5CH_9$/1 mol of product.

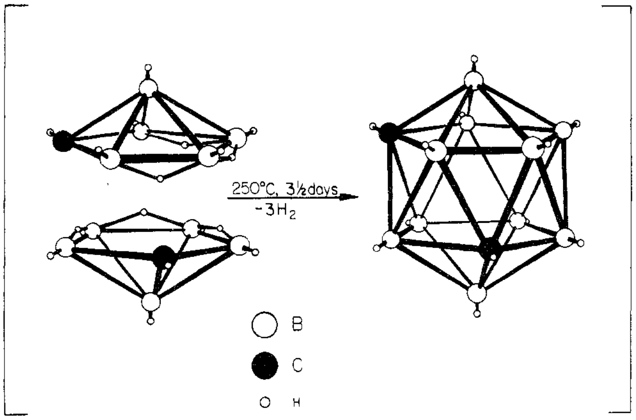

Figure 1. Schematic representation of the fusion of two B_5C skeletons to produce the $1,7\text{-}B_{10}C_2$ skeleton.

form one molecule of *closo*-1,7-dicarbadodecaborane(12). We find unusual the fact that the two nido B_5C cages do not come together with bridge hydrogens apart, thereby generating the $1,12\text{-}B_{10}C_2H_{12}$ species.

One reviewer has proposed the idea that the reacting species may not be $2\text{-}B_5CH_9$ but a nido isomer of B_5CH_7.[5] At the temperature of the pyrolysis reaction simple bridge hydrogen loss from *nido*-$2\text{-}B_5CH_9$ would generate the *nido*-B_5CH_7 isomer. This isomer would retain one bridge hydrogen on the open B_5C skeleton. The area from which the two bridge hydrogens were removed would now have a high electron density and would serve as a center to attack the most electrophilic area (*i.e.*, the carbon atom) on *nido*-$2\text{-}B_5CH_9$ or another *nido*-B_5CH_7. Assuming the lone bridge hydrogen on a *nido*-B_5CH_7 lies opposite the carbon atom, the $1,7\text{-}B_{10}C_2$ skeleton would be uniquely generated. We find this proposal interesting but must add that one might also expect the known *closo*-B_5CH_7[5] to be generated from a *nido*-B_5CH_7. No *closo*-B_5CH_7 is observed, although nido → closo conversions are well known for two-carbon carboranes.[1,2]

A second pathway for decomposition is suggested by the high yield of $1,3\text{-}B_7C_2H_{13}$ and its pyrolysis products $1,7\text{-}B_6C_2H_8$ and $1,6\text{-}B_8C_2H_{10}$.[6] The exact nature of this mechanism is unclear at this time, but it, too, represents a monocarbon to dicarbon carborane conversion. This latter mechanism is apparently the only pathway followed in the pyrolysis of $3\text{-}CH_3B_5CH_8$ (see Experimental Section). Examination of the ^{11}B nmr spectrum of the $1,6\text{-}B_8C_2H_8(CH_3)_2$ recovered revealed only that the two *B*-methyl units were in equatorial positions.

At the present time, few other systems exist to test whether this "fusing" reaction is a general one in boron chemistry. We suggest that $2,3\text{-}B_4C_2H_8$ and B_6H_{10} might fuse to form $1,2\text{-}B_{10}C_2H_{12}$. We also point out that the isostructural molecules, $2,3,4\text{-}B_3C_3H_7$[1] and $2,3,4,5\text{-}B_2C_4H_6$,[7] may prove interesting candidates for future reactions of this kind.

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Registry No. $2\text{-}B_5CH_9$, 12385-35-2; $1,7\text{-}B_6C_2H_8$, 23732-90-3; $1,6\text{-}B_8C_2H_{10}$, 23704-81-6; $1,7\text{-}B_{10}C_2H_{12}$, 16986-24-6; $1,3\text{-}B_7C_2H_{13}$, 49547-48-0; $3\text{-}CH_3B_5CH_8$, 23087-40-3; $1,6\text{-}B_8C_2H_8(CH_3)_2$, 17731-50-9.

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Contribution from the William Rand Kenan, Jr.,
Laboratories of Chemistry, University of North Carolina,
Chapel Hill, North Carolina 27514

Single-Crystal Magnetic Susceptibility Measurements on Tris(ethylenediamine)cobalt(III) Di-μ-chloro-bis[trichlorocuprate(II)] Dichloride Dihydrate. A Compound Which Contains the Dimeric $Cu_2Cl_8^{4-}$ Anion

Kenneth T. McGregor, D. Bruce Losee, Derek J. Hodgson, and William E. Hatfield*

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The preparation of a complex having the empirical formula $Co(en)_3CuCl_5 \cdot H_2O$ (en is ethylenediamine) was reported by Kurnakow[1] in 1898. Recently,[2,3] this compound was found to be structurally unique and consequently it is of unusual chemical interest. The X-ray crystal structure analysis[2] revealed the expected tris(ethylenediamine)cobalt(III) cation, an unexpected $[Cu_2Cl_8]^{4-}$ dimeric anion, along with uncoordinated chloride ions and water molecules. Preliminary magnetic susceptibility measurements[3] on a powdered sample revealed the presence of an exchange interaction between the copper(II) ions. In order to more precisely characterize the exchange interaction and to accurately determine the associated magnetic parameters for this compound, we have undertaken magnetic susceptibility measurements on a single crystal of $[Co(en)_3]_2[Cu_2Cl_8]Cl_2 \cdot 2H_2O$, and the results are reported herein along with additional high-temperature magnetic susceptibility data on a powdered sample.

Experimental Section

Preparation. Reasonably large single crystals of $[Co(en)_3]_2[Cu_2Cl_8]Cl_2 \cdot 2H_2O$ were grown from an aqueous solution containing 3.5 g of $[Co(en)_3]Cl_3$, 1.5 g of $CuCl_2 \cdot 2H_2O$, and 1–2% HCl. In most instances, some starting material ($[Co(en)_3]Cl_3$) recrystallized and was removed before the desired crystals formed.

Anal. Calcd for $[Co(C_2N_2H_8)_3][Cu_2Cl_8]Cl_2 \cdot 2H_2O$: C, 14.47; H, 5.26; N, 16.87. Found (powdered sample): C, 14.56; H, 5.28; N, 16.65. Found (single crystal): C, 14.65; H, 5.40; N, 17.12.

The crystals form as hexagonal prisms whose morphology has been described elsewhere.[2] The hexagonal faces are bounded by the (100) and $(\bar{1}00)$ planes, and the rectangular faces are bounded by the $(01\bar{1})$, $(0\bar{1}1)$, (001), $(00\bar{1})$, (011), and $(0\bar{1}\bar{1})$ planes. The crystals were found to cleave in the *bc* plane.

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Susceptibility Measurements. A crystal with suitable dimensions (~5.2 × 2.9 × 2.5 mm) was mounted with Apiezon N-grease on the (100) face on a Lucite holder such that the magnetic field could be applied along the crystallographic *b* and *c* axes. Susceptibility data were collected for these orientations from 4.2 to 80°K. The crystal was then remounted such that the magnetic field could be applied along the *a* and *b* axes and data collected from 4.2 to 45°K. Some redundant data were collected along the *b* axis and the reproductibility was excellent. Magnetic susceptibility measurements were also made from 130 to 235°K on a polycrystalline sample. Since no field dependence of the susceptibility was detected, all measurements were made with a magnetic field strength of 10 kG.

All susceptibility measurements were made with a Foner-type vibrating sample magnetometer[4] which was calibrated[5] using mercury tetrathiocyanatocobaltate(II) as a standard. Temperatures were measured with a calibrated Ga-As diode. The magnetic field was calibrated by nuclear resonance techniques. All susceptibility data were corrected for the diamagnetism of the constituent atoms using Pascal's constants[6] and for TIP[7] (according to $N\Delta g\beta^2/\lambda = 60 \times 10^{-6}$ cgsu).

Results

The temperature variation of the inverse susceptibility of the polycrystalline sample in the temperature range 130-235°K is shown in Figure 1. The data obey a Curie-Weiss law of the form $\chi = C/(T - \Theta)$ where $C = 0.402$ and $\Theta = +4.2°$. Figure 2a shows the magnetic susceptibility of the single crystal with the magnetic field oriented along the crystallographic *c* axis. The solid line is the best fit to the Bleaney-Bowers equation (*vide post*). The data are seen to maximize with the maximum value of susceptibility measured at 12.9°K. The susceptibility data collected with the field along the *a*, *b*, and *c* axes are shown in Figure 2b. While the data are all very similar, all showing maxima around 13°K, the usual *g*-factor anisotropy is observed. As seen from Figure 2b, $\chi_c > \chi_a > \chi_b$ and the anisotropy is greatest between χ_c and $\chi_{a,b}$.

Discussion

The complex crystallizes in the unique space group P_{bca}-($D_{2h}{}^{15}$) of the orthorhombic system with four dimeric formula units per cell. The dimeric unit is best described as two copper(II) ions in distorted trigonal bipyramidal environments and bridged by one axial chloride and one equatorial chloride. The copper(II)-copper(II) separation within the dimer is 3.722 Å and the Cu(II)-Cl-Cu(II) bridge angle is 95.2°.[2] The unit cell viewed along the *a* axis is shown in Figure 3a (only the dimeric unit is shown). The strictly planar Cu_2Cl_2 unit is seen to be approximately perpendicular to the *a* axis. Figure 3b shows a view of the unit cell along the *c* axis. The copper(II)-copper(II) vector is seen to be almost collinear with the *c* axis. Thus, measurements in these two directions will yield susceptibilities nearly perpendicular and nearly parallel, respectively, to the copper-copper vector. Furthermore, along any particular crystallographic direction all anions are magnetically equivalent with each direction being magnetically unique. Except in the most unfortunate set of circumstances, measurements along these three directions for this complex should reveal any anisotropy in the exchange interaction. The susceptibilities measured are the principal values, since the principal susceptibility values are constrained to be along the crystallographic axes[8] in orthorhombic symmetry.

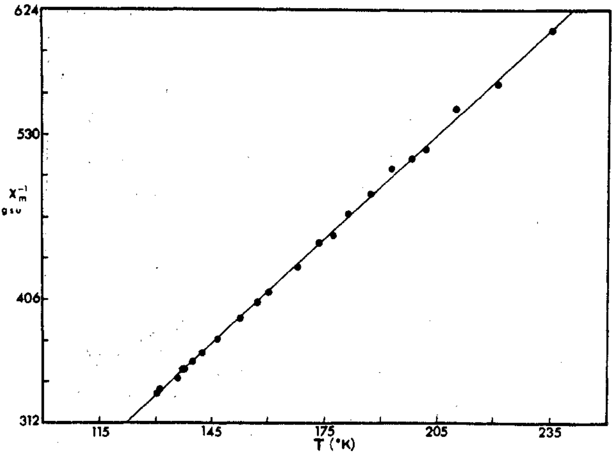

Figure 1. The high-temperature variation of the inverse magnetic susceptibility of the polycrystalline sample (●). The solid line shows the Curie-Weiss behavior at high temperatures.

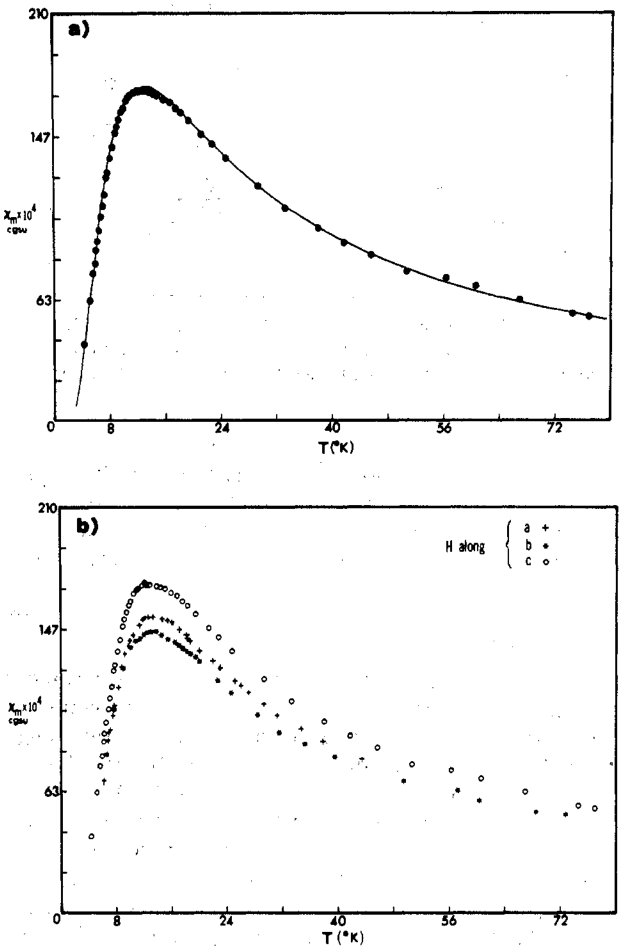

Figure 2. (a) The low-temperature magnetic susceptibility of the single crystal along the *c* axis (●). The solid curve was generated from eq 2 with the following parameters: $g_c = 2.18$, $J/k = -10.6°$, and $J' = 0.0$. (b) The low-temperature magnetic susceptibility of the single crystal for orientations along the *a* (+), *b* (*), and *c* (o) crystallographic directions.

The inverse susceptibility plot in Figure 1 gives a Curie constant of 0.402 which yields an average *g* value of 2.08 calculated according to

$$g^2 = \frac{3kC}{N\beta^2 S(S+1)} \qquad (1)$$

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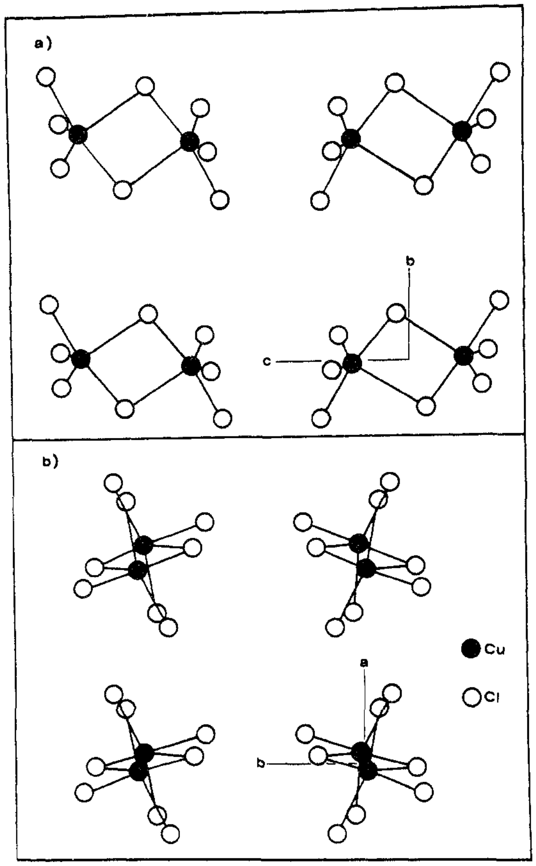

Figure 3. Projections of the unit cell of $[Co(en)_3][Cu_2Cl_8]Cl_2 \cdot 2H_2O$ showing only the dimeric $Cu_2Cl_8{}^{4-}$ ions: (a) a projection on the crystallographic *bc* plane; (b) a projection on the crystallographic *ab* plane.

The full curve in Figure 2a is the best fit to the modified Bleaney-Bowers expression[9,10] for exchange coupled copper(II) dimers which results from the application of the Heisenberg exchange Hamiltonian $\mathcal{H} = -2J\mathbf{S}_1 \cdot \mathbf{S}_2$. The symbols in (2) have their usual meaning; J' represents the exchange in-

$$\chi_m = \frac{Ng^2\beta^2}{kT(3 + e^{-2J/kT}) - 4ZJ'} \qquad (2)$$

teraction between Z nearest neighboring dimers according to molecular field theory. The theoretical curve in Figure 2a fits the experimental data over the entire temperature range very well, with only 5 of the 44 data points differing by more than 1.5% from the calculated values and with 34 of the 44 data points differing by less than 1%. The data for the other two directions were fitted with comparable precision. The following parameters along the ith directions ($i = a$, b, and c) were extracted from the data: $J_a/k = -10.7 \pm 0.2°$ and $g_a = 2.07 \pm 0.02$; $J_b/k = -10.8 \pm 0.2°$ and $g_b = 2.03 \pm 0.02$; $J_c/k = -10.6 \pm 0.2°$ and $g_c = 2.18 \pm 0.02$. No significant improvement in the fit was observed when nonzero values for J' were included (*vide infra*). Hence, within the experimental error, $J_a = J_b = J_c = J$. The average value of g, calculated by $\langle g \rangle = (1/3)(g_a + g_b + g_c)$, is 2.09, a value which is in excellent agreement with the result obtained from the polycrystalline data.

Thus, the exchange interaction observed along the c axis, which is almost collinear with the copper(II)-copper(II) vector, and the exchange interaction observed along the a and b axes, which are almost perpendicular to the copper(II)-copper(II) vector, are equal in magnitude. It should also be noted that the introduction of nonzero values for J' did not improve the fit of eq 2 to the experimental data. This indicates that there is no significant long range interdimer exchange present in the system. This result is not unexpected in view of the large interdimer separation.[2]

Table I. Magnetic and Structural Data for Chloro-Bridged Trigonal Bipyramidal Copper(II) Dimers

Compd	$2J$, cm^{-1}	Cu-Cl-Cu angle, deg	Cu-Cl in-plane, Å	Cu-Cl out-of-plane, Å	Ref
$Cu_2Cl_8{}^{4-}$	−14.6	95.2	2.70	2.33	2, This work
$[Cu(guaninium)Cl_3]_2$	−83	98	2.45	2.29	11, 12

The large copper(II)-copper(II) separation of 3.722 Å precludes any through-space interactions since no significant orbital overlap can occur over this distance, and dipole-dipole interactions could not produce a splitting of the observed magnitude. Hence, it seems reasonable to conclude that the interaction occurs *via* superexchange through the chloride bridges.

It is of interest to compare the magnetic parameters and structural data given in Table I for the $[Cu_2Cl_8]^{4-}$ dimeric anion with comparable data for the structurally similar magnetically characterized chloro-bridged bimetallic copper(II) complex,[11,12] di-μ-chloro-bis[dichloroguaniniumcopper(II)]. These complexes are made up of pairs of trigonal bipyramids sharing equatorial to apex edges. It is likely that the unpaired electrons are in the copper d_{z^2} orbitals in the single ion ground states. The larger singlet-triplet splitting for $[Cu(guaninium)Cl_3]_2$ in comparison to $[Cu_2Cl_8]^{4-}$ accompanies an increase in the Cu-Cl-Cu angle from 95.2 to 98° and a shortening of the copper-chloride bonds. It has been demonstrated that the angle at the bridge is of prominent importance in determining the sign and magnitude of $2J$ in a series of hydroxo-bridged copper(II) complexes;[13] it is not clear, however, that the trend observed for the hydroxo-bridged complexes should be followed in the present situation, since the structures are different and the exchange coupling mechanisms involve different orbitals. Furthermore, an additional complication is pressed on the chloride-bridged systems by the rather dramatic changes in bond distances. The copper-oxygen bond distances in the hydroxo-bridged systems are nearly constant at 1.90-1.94 Å,[14-17] while as shown in Table I the copper-chlorine bond distances range from 2.29 to 2.70 Å for these trigonal bipyramidal dimers. This observation invites a search for additional cop-

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per dimers so that the bond length effect can be separated from the bridge angle effect.

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Registry No. $[Co(en)_3]_2[Cu_2Cl_8]Cl_2 \cdot 2H_2O$, 28852-88-2.

Contribution from the Department of Cheimstry and
Polymer Research Institute, University of Massachusetts,
Amherst, Massachusetts 01002, and Hercules Research Center,
Wilmington, Delaware 19899

Electron Paramagnetic Resonance of Tetrakis(1-norbornyl)vanadium and -cobalt[1]

B. K. Bower,[2a] M. Findlay,[2b] and James C. W. Chien*[2b]

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Many soluble transition metal peralkyls display inconvenient degrees of thermal, oxidative, and hydrolytic stability. Pure $(Me)_4Ti$ thermally decomposes at room temperature, and $(Et)_4Ti$ is less stable. Peralkyl transition metal compounds which must pass through relatively high energy transition states in order to decompose by metal hydride elimination,[3-5] such as (benzyl)$_4$V,[6] $(Me_3SiCH_2)_4Cr$,[7] $(Me)_6W$,[8] $(Me_3CCH_2)_4Ti$,[9] (benzyl)$_4$Zr,[10] and (t-Bu)$_4$Cr,[11] are more thermally stable. However reactions of the above-mentioned compounds with moisture and oxygen are facile. By far the most stable known transition metal peralkyls are 1-norbornyls of first row transition elements. The absence of hydrogen on α carbons and the inability to form a reasonable π bond at the bridgehead preclude metal hydride elimination, while the bulky norbornyl groups shield the metal and the metal-carbon bonds from attack by external reagents.[12]

(nor)$_4$Cr has a $3d^2$ configuration and its epr spectra in various environments have been described.[13] In this paper we describe the epr results of (nor)$_4$V and (nor)$_4$Co.

Experimental Section

The synthesis of (nor)$_4$V and (nor)$_4$Co follow procedures analogous to that given for (nor)$_4$Cr.[11-13] The epr spectra were obtained with a Varian E-9 spectrometer operating in the X-band frequency. Other aspects of the experimental methods have been given previously.[13]

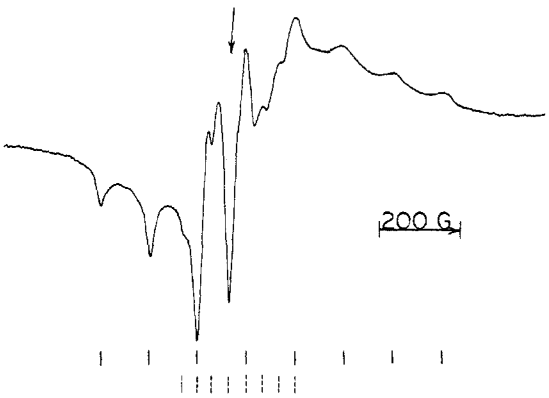

Figure 1. Epr spectrum of (nor)$_4$V 60 mM in pentane at 77°K. Marker is for DPPH.

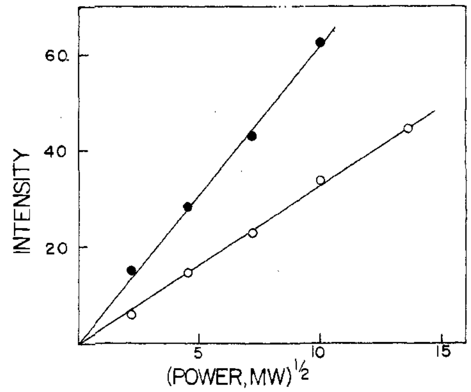

Figure 2. Saturation curve: ●, (nor)$_4$V 60 mM in pentane at 77°K; ○, (nor)$_4$Co 10.4 mM in benzene at 298°K.

The (nor)$_4$V solutions used were 50 mM in isooctane and 60 mM in n-pentane. The (nor)$_4$Co solutions studied were 10.4 mM in benzene, 12.5 mM in isooctane, 7.3 mM in n-heptane, and 9.3 mM in cyclohexane.

Results and Discussion

(nor)$_4$V has a $3d^1$ configuration. Its ground state in a tetrahedral ligand field is ^2E. A distortion of trigonal symmetry does not split levels of e symmetry. However, with a distortion of tetragonal symmetry or lower, the ground state is ^2B for an elongated tetrahedron and ^2A for compressed tetragonal symmetry. (nor)$_4$Co was shown to be a low-spin complex.[12] It has a ^2T ground state which becomes ^2E under a tetragonal compression or $^2B_2$ under a tetragonal elongation.

(nor)$_4$V has no detectable epr signal at temperatures down to 143°K. Below this temperature an epr signal becomes discernible. Figure 1 shows the spectrum obtained at 77°K; it is the same in all the solvents studied. The spectral parameters are $g_\perp = 1.984$, $g_\parallel = 2.036$, $|A_\perp| = 120$ G, and $|A_\parallel| = 40$ G. The relaxation time of (nor)$_4$V is still quite short at 77°K; the resonance is not saturated at 200-mW microwave power (Figure 2).

The spin-lattice relaxation time of (nor)$_4$Co is much longer than that of (nor)$_4$V. A room-temperature epr spectrum was observed with $g = 2.1316$ and ΔH (line width) = 135-140 G. Though the spectrum is the same in all the solvents studied at room temperature, the low-temperature spectrum is dependent on the medium. In benzene, the 298 and 77°K epr spectra are the same aside from the expected (2-3)-fold increase in intensity. In n-heptane and isooctane, the spec-

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