prepared by means of a coupling reaction which generates a boron–boron bond. In a system of this sort, in which ternary boron is in the presence of potential nucleophiles such as nitrogen and chlorine in unreacted chloroborane, structural rearrangement to the fused cyclic ring system can be envisioned through a four-center mechanism.

Experimental Section

Mass Spectra.—An Associated Electrical Industries MS-902 mass spectrometer operating at 70 eV was used to obtain mass spectra. Solid samples were introduced *via* a direct insertion probe. A heated inlet system was employed for liquid samples. Heptacosafluorotributylamine was used as a standard in exact mass determinations.

Materials.—All samples were handled by conventional vacuum line and drybox techniques. A complementary sample of $B_2[N(CH_3)_2]_4$ was obtained from U. S. Borax Research Corp. The compounds $B_2(OCH_3)_4$, $B_2(O_2C_2H_4)_2$, $B_2(S_2C_2H_4)_2$, and $B_2[N_2(CH_3)_2C_2H_4]_2$ were prepared using methods described previously in the literature.[1,5]

$B_2(SCH_3)_4$.—In a typical experiment, 6.88 mmol of $B_2[N(CH_3)_2]_4$ was dissolved in 40 ml of CH_2Cl_2 in a 100-ml bulb. Slight excesses (28.00 mmol) each of CH_3SH and HCl were added to the solution at −95°. The bulb was allowed to warm to room temperature over a 4-hr period and stirred continuously for 12 hr. The solvent was removed by fractional distillation at −45°. $B_2(SCH_3)_4$, bp 115° (1–2 mm), a clear colorless liquid, was distilled from the reaction bulb leaving behind a crystalline white solid identified as $(CH_3)_2NH_2Cl$ by its X-ray powder pattern; yield, 95% based upon the amount of salt recovered.

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The Infrared and Raman Vibrational Spectra and Structure of Potassium *sym-trans*-μ-Ethyleno-bis(pentacyanocobaltate(III))

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In a continuation of our spectroscopic studies on coordination compounds and specifically on compounds with bridging ligands,[1] we have investigated the infrared and Raman spectra of potassium *sym-trans*-μ-ethylenobis(pentacyanocobaltate(III)). Its resemblance to one possible structure of the "red" isomer of the pentaminenitrosylcobalt ion is obvious. One difficulty encountered with the latter compound was the assignment of a possibly symmetrical N–N stretching frequency to a rather strong infrared band. If this ion did contain a *sym-trans*-μ-hyponitrito linkage, this band would be expected to be infrared forbidden. It has so far been impossible to carry out a Raman study using the present laser source, which causes decomposition. It was hoped that through the present study further information could also be obtained involving the structural assignment of the "red" isomer.

The dipentacyanocobalt–ethylene complex could have either the *cis* or *trans* structure. Using steric considerations the *cis* isomer seems unlikely as pointed out in its initial investigation.[2] However, a strong band at 1622 cm^{-1} was assigned to the C–C stretching mode. Through a complete vibrational analysis involving deuterium-substituted species, we hoped to establish the configuration of this complex.

Experimental Section

Potassium *sym-trans*-μ-ethyleno-bis(pentacyanocobaltate(III)) was prepared as reported by Griffith and Wilkinson.[2] We were also able to prepare the identical compound through the reaction of acetylene and the hydridopentacyanocobalt(II) ion.[3] The deuterated compound was prepared by carrying out the preparation in D_2O carefully excluding all H_2O. It was hoped that the compound could be prepared with the four waters of crystallization as D_2O and separately with the deuterated ethylenic linkage, but due to exchange this was impossible. The entire system was deuterated using C_2D_2 prepared from calcium carbide and D_2O.

The Raman spectra were recorded on a Cary Model 81 spectrophotometer equipped with a 6328-Å He–Ne laser source. Samples were run only as solids, because the solutions decomposed in the laser beam. The infrared spectra were recorded from 4000 to 200 cm^{-1} using a Beckman IR-12 spectrophotometer with the calibration checked in the usual manner.[4,5] Samples were examined as Nujol mulls on KBr plates as well as in KBr and CsI disks. The very far-infrared spectra were recorded on a Beckman IR-11 utilizing samples prepared as Nujol mulls supported between polyethylene plates. Both instruments were purged with dry air. Sharp bands are expected to be within ±2 cm^{-1}.

Analyses for the compound were performed by Galbraith Laboratories, Knoxville, Tenn. *Anal.* Calcd for $K_6[Co(CN)_5]_2C_2H_2\cdot 4H_2O$: C, 20.3; H, 1.7; N, 19.7. Found: C, 19.0; H, 1.7; N, 20.0. There was no sign of decomposition during the recording of the spectrum. A check was also made for strong bands from $K_3[CO(CN)_6]$.

Results and Discussion

The infrared and Raman spectra of $K_6[Co(CN)_5]_2C_2H_2\cdot 4H_2O$ and $K_6[Co(CN)_5]_2C_2D_2\cdot 4D_2O$ were recorded from 4000 to 50 cm^{-1}. This compound is expected from steric considerations to have C_{2h} symmetry about the ethylene linkage and C_{4v} symmetry about each cobalt atom. From the infrared and Raman studies on this compound and its deuterated analog, it was possible unequivocally to confirm these expectations.

Infrared and Raman Spectral Assignment.—In order to simplify the band assignments, they will be divided into those associated with the *trans*-ethylenic linkage followed by those from the metal and its coordinated atoms.

Assignments for the fundamental frequencies in the ethylenic linkage are presented in Table I. These assignments are in excellent agreement with the absorption bands previously reported for the *trans*-dihalo-

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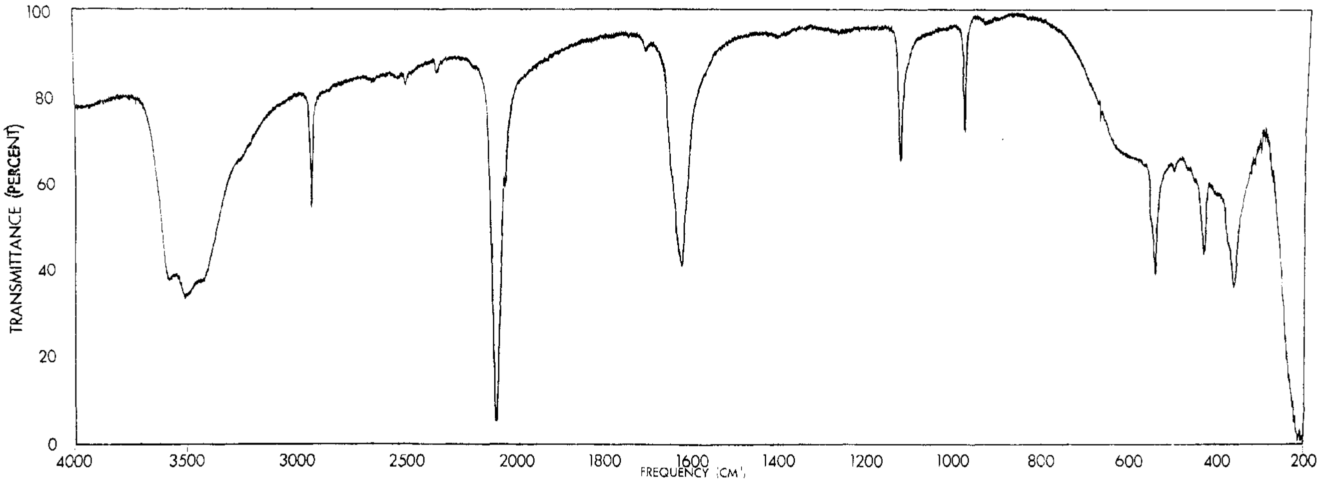

Figure 1.—Infrared spectrum of $K_6[Co(CN)_5]_2C_2H_2 \cdot 4H_2O$.

ethylene compounds[6-8] and are the basis for the present assignments. The 1518-cm^{-1} band is assigned to ν_2, the C=C stretching fundamental, since it shifts only slightly upon deuteration.

TABLE I
VIBRATIONAL SPECTRAL DATA FOR ETHYLENIC COMPOUNDS[a]

		$C_2H_2Cl_2$[8]	$C_2H_2Br_2$[9]	$K_6[Co_2(CN)_{10}$-$C_2H_2] \cdot 4H_2O$	$K_6[Co_2(CN)_{10}$-$C_2D_2] \cdot 4D_2O$	$C_2D_2Br_2$[9]
				Raman		
Ag	ν_1	3073 s	3089 m	2940 m	2206 w	2323 m
	ν_2	1578 s	1581 m	1518 vs	1506 s	1531 m
	ν_3	1274 s	1249 vs	1237 vs	952 vs	972 s
	ν_4	846 s	746 s	632 vs	586 s	670 m
	ν_5	350 s	216 vs	144 s	143 s	214 vs
Bg	ν_8	763 m	736 w	735 w	635 w	628 w
				Infrared		
Au	ν_6	895 vs	898 vs	973 m	725 m	658 s
	ν_7	227 m	188 w	157 w	. . .	183 w
	ν_9	3080 s	3085 vs	2942 m	2182 m	2289 vs
Bu	ν_{10}	1200 s	1165 s	1123 m	834 m	858 s
	ν_{11}	817 vs	680 vs	366 m	365 m	648 m
	ν_{12}	250 w	192 w	172 m	. . .	194 w

[a] Abbreviations used: s, strong; m, medium; w, weak; v, very.

The assignment of the bands at 2940, 1237, 632, and 735 cm^{-1} to ν_1, ν_3, ν_4, and ν_8, respectively, was clearly established from the deuterium isotope shifts. ν_5 was assigned to a very intense Raman band at 144 cm^{-1} on the basis of its intensity and combinations found in the infrared spectrum.

The infrared fundamentals were assigned similarly to the Raman bands. The bands at 975, 2942, and 1123 cm^{-1} are ν_6, ν_9, and ν_{10}, respectively. Modes ν_7, ν_{11}, and ν_{12} are essentially motion independent of the hydrogens and do not shift significantly upon deuteration. Furthermore, ν_7 and ν_{12} are reported as weak bands in the previous spectral studies[7,9] and are probably below the limits of normal instrumentation. There is a pair of bands at 157 and 172 cm^{-1} which cannot be explained as any fundamental in the $Co(CN)_5$ part of the molecule from previous work on $K_3[Co(CN)_6]$.[10-13] On this basis these bands are suggested to arise from ν_7 and ν_{12}, respectively. It is felt that a reasonable assignment for the frequency of ν_{11} at 366 cm^{-1} can be made on the basis of a small isotopic shift and combination bands. Again a comparison of this work to $K_3[Co(CN)_6]$ shows this to be the only significant new band in this far-infrared region.

The infrared spectrum of $K_6[Co(CN)_5]_2C_2H_2 \cdot 4H_2O$ is shown in Figure 1. The tabulated data are presented in Table II. The assignments in the higher frequency region are reasonably straightforward from work done previously.[10-14] The disputed band[2] at 1622 cm^{-1} is made up of the δ(H–O–H) mode plus a strong combination arising from the $\nu_6 + \nu_4$[8] bands in the ethylenic linkage. It was possible to see a very weak absorption

TABLE II
INFRARED DATA OF $K_6[Co(CN)_5]_2C_2H_2 \cdot 4H_2O$[a]

Cm^{-1}	Intens	Assignment	Cm^{-1}	Intens	Assignment
3590	s	H_2O str	975	m	ν_6
3510	vs	H_2O str	583	sh	MCN bend
3440	sh	H_2O str	543	m	MCN bend
2942	m	C—H str	500	vw	144 + 360
2650	vw	543 + 2115	468	vw	Combination
2540	vw	432 + 2115	455	sh	M—CN str
2500	w	432 + 2092	432	m	M—CN str
2200	vw	78 + 2128	400	sh	Combination
2115	s	C≡N str	375	sh	Combination
2092	vs	C≡N str	366	m	ν_{11}
2050	sh	^{13}C≡N str	184	sh	Combination
1709	w	$\nu_6 + \nu_8$	172	m	ν_{12}
1645	sh	1517 + 144	157	w	ν_7
1622	s	H_2O bend	146	bs	H_2O librations
1530	vvw	ν_2	56	m	Lattice
1123	m	ν_{10}			

[a] Abbreviations used: s, strong; m, medium; w, weak; v, very; sh, shoulder; b, broad.

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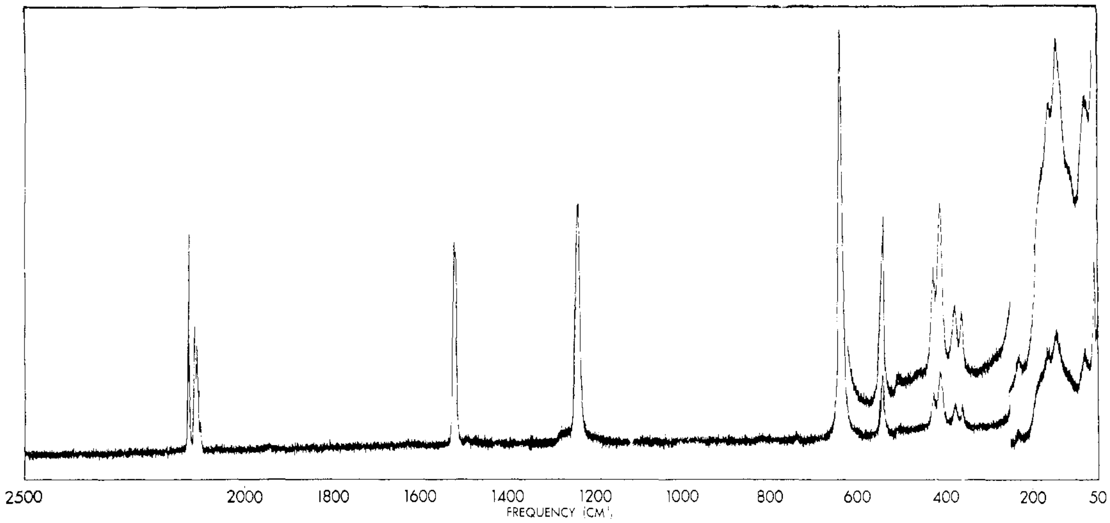

Figure 2.—Raman spectrum of solid $K_6[Co(CN)_5]_2C_2H_2 \cdot 4H_2O$.

at 1530 cm^{-1} which does agree favorably with the Raman data for the C=C stretching frequency ν_2. There are several bands below 200 cm^{-1} in the far-infrared region. These could be combinations of other low-frequency bands, crystal lattice modes or the vibrations ν_7 and ν_{12} as suggested. There has been an attempt at least to suggest some possibilities for the appearance of the very weak bands in the spectrum. The band at 1530 cm^{-1} in the infrared region has been proposed to arise from the ν(C=C) vibration which may be slightly activated by site symmetry; it may indeed be a combination band.

The Raman spectrum is presented in Figure 2 for potassium *sym-trans-μ*-ethyleno-bis(pentacyanocobaltate(III)). Table III is a listing of the bands in the spectrum of the normal complex. The assignment of the Raman shifts are more difficult because of a lack of previous work reported in the literature. The 2128- and 2114-cm^{-1} bands are obviously from ν(C≡N). The band at 539 cm^{-1} is most puzzling as are the splittings in the other bands. The relationship between these bands and the infrared bands forces the proposal that these bands are appearing due to the site symmetry of the molecule in the crystal lattice, causing a splitting of the 366-cm^{-1} band. If so, the 539-, 424-, and the 359- and 374-cm^{-1} bands can be related to the infrared bands at 543, 432, and 366 cm^{-1}, respectively. The band at 409 cm^{-1} is the M–CN stretching frequency with the bending frequency at 504 cm^{-1}. This is in agreement with assignments for the spectrum of $K_3[Co(CN)_6]$,[15] previously determined from combination bands in the infrared spectrum.

TABLE III
RAMAN DATA OF $K_6[Co(CN)_5]C_2H_2 \cdot 4H_2O$[a]

Cm^{-1}	Intens	Assignment	Cm^{-1}	Intens	Assignment
2940	m	ν_1, C—H str	632	vs	ν_4
2128	vs	C≡N str	539	s	M—C≡N bend
2114	s	C≡N str	504	vw	M—C≡N bend
2105	s	C≡N str	424	wsh	
2097	sh	C≡N str	409	s	M—CN str
1518	vs	ν_2, C=C str	374	w	M—CC str
1492	vw		359	w	M—CC str
1474	vvw	$2\nu_8$	226	vw	
1237	vs	ν_3	162	w	
1192	vw		144	s	ν_5
735	w	ν_8	78	vw	Lattice
675	wsh				

[a] Abbreviations used: s, strong; m, medium; w, weak; v, very; sh, shoulder.

Summary and Conclusions

The assignments for the bands in the ethylenic linkage are rather satisfying except for ν_7 and ν_{12}. In all, the spectrum clearly shows the complex to be *trans* as expected from steric considerations. One important point mentioned earlier is the similarity in structure between $K_6[Co(CN)_5HCCHCo(CN)_5]$ and $[Co(NH_3)_5ONNOCo(NH_3)_5](NO_3)_4$, if the latter is *trans*-hyponitrito bridged with the nitrogens coordinated. The probability of this structure for the hyponitrito complex, which was discounted in our earlier study, is further disproved by this study. The basis for this conclusion is the strong band resulting predominantly from the N–N stretching mode found in the spectrum. As in the ethylenic complex there should be no infrared-active stretching frequency at this center of symmetry. It, therefore cannot have a center of symmetry.

The M–CC stretching mode is assigned to the band at 370 cm^{-1}. There are few data on transition metal–carbon stretching frequencies for systems containing a normal covalent M–C bond other than for platinum and palladium.[16]

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