pounds with transfer RNA have already been performed,[7,8,33] and further work is in progress.

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Registry No. Bis(6-mercapto-9-benzylpurine)palladium-dimethylacetamide, 50306-73-5; bis(6-mercapto-9-benzylpurine)-platinum-dimethylacetamide, 50306-74-6.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-815.

(33) (a) B. C. Pal, L. R. Shugart, K. R. Isham, and M. B. Stulberg, *Arch. Biochem. Biophys.*, 150, 86 (1972); (b) A. S. Jones, R. T. Walker, and V. Youngs, *Biochim. Biophys. Acta*, 299, 293 (1973).

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Transition Metal Hydroborate Complexes. VII.[1] Preparation, Properties, and Structure of Bis(cyanotrihydroborato)-1,1,4,7,7-pentamethyldiethylenetriaminecopper(II)

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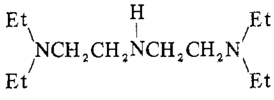
The compound bis(cyanotrihydroborato)-1,1,4,7,7-pentamethyldiethylenetriaminecopper(II) has been prepared and its crystal and molecular structure determined by a single-crystal X-ray diffraction study. The complex crystallizes in the space group *Pbca* of the orthorhombic system with eight monomeric molecules in the unit cell. Lattice parameters are $a = 14.749$ (2) Å, $b = 17.604$ (3) Å, and $c = 13.907$ (3) Å. Using 1391 unique observed reflections collected by diffractometer, the structure was solved and refined on F to a final value for the discrepancy index R_1 of 0.031. The compound is a pentacoordinate complex of copper(II). The coordination polyhedron is a distorted square-based pyramid with one of the $-NCBH_3$ ligands occupying the apical position. The two Cu-N distances to the cyanotrihydroborate ligands are 1.980 (4) and 2.153 (3) Å (apical) and the Cu-N-C bond angles are 165.0 (3) and 175.6 (3)°, respectively. The difference in bonding of the two $-NCBH_3$ ligands can account for the appearance of the two CN stretching frequencies separated by 18 cm^{-1} which are observed in the infrared spectrum of the solid. The molar conductivity of this complex at 25° in several solvents and its magnetic susceptibility as a function of temperature have been investigated and are discussed in terms of the known structure.

Introduction

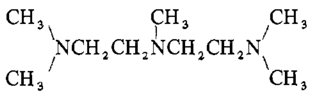
The use of the cyanotrihydroborate anion to produce complexes containing the $M-NCBH_3$ linkage has been the subject of several recent investigations.[3-7] The structure of a copper(I) complex in which H_3BCN^- acts as a bidentate bridging ligand has recently been determined in these laboratories.[1] Interest in the present compound grew out of a study, currently in progress, to prepare and characterize complexes in which the cyanotrihydroborate anion serves to bridge paramagnetic metal ions.

It is well known[8-11] that the two tridentate ligands 1,1,4,7,7-pentamethyldiethylenetriamine (Me_5dien) and 1,1,7,7-tetraethyldiethylenetriamine (Et_4dien) frequently form pentacoordinate complexes of the first-row transition elements.



$(Et)_2NCH_2CH_2N(H)CH_2CH_2N(Et)_2$

Et$_4$dien



$(CH_3)_2NCH_2CH_2N(CH_3)CH_2CH_2N(CH_3)_2$

Me$_5$dien

Copper(II) usually prefers a coordination number of 6. The alkyl substituents on the triamine ligand cause pronounced stereochemical effects, however, and the extra bulk tends to block the sixth coordination site and produce pentacoordinate copper. The structure of the complex formed by copper(II) with Me_5dien and the cyanotrihydroborate anion was therefore anticipated to be either the dimeric cation $[Cu(Me_5dien)(NCBH_3)]_2^{2+}$ or the neutral $Cu(Me_5dien)(NCBH_3)_2$. The present investigation distinguishes between these two possibilities and provides further structural information about the cyanotrihydroborate ion as a ligand.

Experimental Section

Synthesis. A 1.59-g (9-mmol) sample of Eastman 1,1,4,7,7-pentamethyldiethylenetriamine (Me_5dien) dissolved in 50 ml of 95% ethanol was added to 2.0 g (9 mmol) of copper(II) bromide dissolved in 400 ml of 95% ethanol, with continuous stirring. On mixing, the brown cupric bromide solution darkened and then became a deep blue. A 1.49-g (>18-mmol) amount of Aldrich sodium cyanotrihydroborate was added to 250 ml of 95% ethanol and stirred for several minutes. Dissolution was incomplete and the mixture was filtered into the deep blue cupric solution while stirring continuously. A further darkening of the blue solution was observed. The solution was stirred for 2 hr at room temperature and then chilled in an ice bath. A very small amount (0.04 g) of an insoluble greenish blue

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(1) Part VI: K. M. Melmed, T. Li, J. J. Mayerle, and S. J. Lippard, *J. Amer. Chem. Soc.*, 96, 69 (1974).

(2) (a) Barnard College. (b) Columbia University.

(3) S. J. Lippard and P. S. Welcker, *Chem. Commun.*, 515 (1970).

(4) P. C. Ford, *Chem. Commun.*, 7 (1971).

(5) L. Vaska, W. V. Miller, and B. R. Flynn, *Chem. Commun.*, 1615 (1971).

(6) S. J. Lippard and P. S. Welcker, *Inorg. Chem.*, 11, 6 (1972).

(7) D. G. Holah, A. N. Hughes, B. C. Hui, and K. Wright, *Inorg. Nucl. Chem. Lett.*, 9, 835 (1973).

(8) M. Ciampolini and G. P. Speroni, *Inorg. Chem.*, 5, 45 (1966).

(9) Z. Dori, R. Eisenberg, and H. B. Gray, *Inorg. Chem.*, 6, 483 (1967).

(10) M. DiVaira and P. L. Orioli, *Inorg. Chem.*, 8, 2729 (1969).

(11) R. F. Ziolo, M. Allen, D. D. Titus, H. B. Gray, and Z. Dori, *Inorg. Chem.*, 11, 3044 (1972).

powder was separated by filtration, and solvent was then removed from the deep royal blue filtrate by rotary evaporation at room temperature until the final volume was approximately 50 ml. After suction filtration 2.24 g of deep royal blue crystals was obtained (yield of crude product: 77.2%). The compound was recrystallized by dissolving it in 200 ml of warm (below boiling) methanol and filtering to remove a small amount of insoluble greenish blue powder. Methanol was then allowed to evaporate from the filtrate slowly, at room temperature, over a period of several days; yield 1.324 g (45.6%) of dark blue needles. Microchemical analysis was performed by Galbraith Laboratories, Knoxville, Tenn. *Anal.* Calcd for $C_{11}H_{29}N_5B_2Cu$: C, 41.74; H, 9.23; N, 22.12. Found: C, 41.61; H, 9.22; N, 22.06.

The compound decomposes on heating between 127 and 133°. Gas bubbles are observed to evolve, and the melt is greenish blue. The compound is soluble in alcohols and polar solvents such as water, acetonitrile, methanol, ethanol, and 2-propanol. It is insoluble in CS_2, benzene, toluene, diethyl ether, and chloroform. It decomposes in acetone upon standing for approximately 20 min.

Physical Measurements. The magnetic susceptibility was measured by the Faraday method using a Model 1423 Alpha Scientific magnetic susceptibility system with a variable-temperature cryostat and an Ainsworth Model 1071 electronic balance. Electrical conductance measurements were carried out at 25.0 ± 0.1° using an Industrial Instruments Model RC-18 conductivity bridge and a cell with platinized platinum electrodes which had a cell constant of 0.145 cm^{-1} (standardized with 0.01 *D* KCl). Infrared spectra were obtained with a Perkin-Elmer 467 grating spectrophotometer in the range 4000–250 cm^{-1}. Samples were mulled in Nujol and spread between either NaCl or KBr plates. Polystyrene was used as the calibrant and the resulting frequencies are estimated to be accurate to ±2 cm^{-1}. Optical spectra were obtained in methanol solution using a Beckman DBG recording spectrometer and a Beckman DU spectrometer modified with a Gilford Model 222 photometer.

Collection and Reduction of the X-Ray Data. A dark blue crystal was mounted with nail polish on the end of a glass fiber and transferred to a precession camera to obtain unit cell and space group information using Cu $K\bar{\alpha}$ radiation (λ 1.5418 Å). The crystal was observed to have Laue symmetry *mmm* with extinctions $0kl$, $k \neq 2n$, $h0l$, $l \neq 2n$, and $hk0$, $h \neq 2n$, which uniquely indicate the space group to be $D_{2h}{}^{15}$-*Pbca*.[12]

The crystal was then mounted on a Picker FACS-I-DOS diffractometer and several open-counter ω scans were performed. Although the mosaic spread was suitably low ($\Delta\omega_{1/2} \approx 0.02$–$0.07°$), small shoulders were observed on some of the peaks. Approximately ten other crystals were mounted and in all cases ω scans at a takeoff angle of 0.7° showed structure on some of the peaks. Therefore a new batch of crystals was grown, using water instead of CH_3OH for recrystallization. One of these was mounted and open-counter ω scans of six different peaks displayed no structure. The mosaic spread was acceptably low (~0.03–0.09°), and this crystal was therefore used for data collection.

Lattice parameters $a = 14.749 \pm 0.002$ Å, $b = 17.604 \pm 0.003$ Å, and $c = 13.907 \pm 0.003$ Å were determined at room temperature (*ca.* 23°) by a least-squares refinement of the setting angles ω, χ, and 2θ for 12 reflections ($33° < 2\theta < 69°$) which were carefully centered on the Cu $K\alpha_1$ line (λ 1.54041 Å). The refinement used the logic of the FACS-I-DOS system.[13] The calculated density, assuming eight $(Me_5dien)Cu(NCBH_3)_2$ molecules per unit cell, is 1.164 g/cm³. The experimental density measured by flotation in a mixture of *n*-pentane and CCl_4 was 1.17 ± 0.01 g/cm³, in good agreement with the crystallographic value.

Intensity data were obtained with Ni-filtered Cu $K\bar{\alpha}$ radiation using a symmetric scan range of 1.30° in 2θ plus the $K\alpha_1 - K\alpha_2$ difference. The takeoff angle at the X-ray tube was 2.2° and an aperture of 5.0 × 5.0 mm was placed in front of the scintillation counter at a distance of about 31 cm from the crystal. Stationary-crystal, stationary-counter background counts of 10-sec duration were taken at the beginning and end of the scan range. Aluminum foil attenuators of various thickness were automatically inserted in front of the counter aperture whenever the counting rate exceeded 10,000 counts/sec in order to prevent saturation of the counter circuit. Three standards, well separated in their angular settings, were collected every 60 reflections. The average intensities of the three standard reflections decreased linearly over the 140-hr collection period by approximately 10% of the original values, and therefore a correction for decomposition was applied to the intensity data. A total of 2174 data (including 285 systematic absences) were collected out to $2\theta < 100°$. Of these, 1391 unique data were judged to be observed by the criterion $F^2 > 3\sigma(F^2)$. The value for $\sigma(F^2)$ was obtained from the expression[14] $\sigma(F^2) = (Lp)^{-1}[E + (t_c/2t_b)^2(B_1 + B_2) + (\epsilon I)^2]^{1/2}$ in which E is the total integrated counts, $t_c/2t_b$ is the ratio of the time spent counting the integrated peak intensity to the total background counting time, B_1 and B_2 are the individual background counts, ϵ is the "ignorance factor" which was set equal to 0.04 to prevent excessively high weights being given to the strong reflections, $I = E - (t_c/2t_b)(B_1 + B_2)$, and $(Lp)^{-1}$ is the Lorentz–polarization factor. The intensities, I, were corrected for Lp effects but not for absorption. The linear absorption coefficient was low (16.8 cm^{-1})[15] and the crystal had approximate dimensions 0.32 × 0.2 × 0.1 mm. Transmission coefficients were estimated to range from 0.737 to 0.814.[16]

Scattering factors used were for the neutral atoms and, for all atoms other than H, were taken from Hanson, *et al.*[17] The scattering factors for H were taken from Stewart, *et al.*,[18] and were calculated for a bonded hydrogen in the H_2 molecule, using a spherical approximation.

Corrections for anomalous dispersion effects for the Cu atoms were taken from the compilation of Cromer[19] and applied to the calculated structure factor amplitudes. The data were placed on an approximately absolute scale through a modification of Wilson's method[20] which produced an estimated mean B of 4.85 Å².

Determination and Refinement of the Structure.[21] An origin-removed Patterson map was computed using the corrected data. From this map it appeared that the compound was monomeric since the shortest Cu–Cu distance was approximately 8.0 Å. Only the copper atoms could be located from the Patterson map. A difference Fourier map based on phases assigned after a least-squares refinement of the scale factor and the Cu atom positional and thermal parameters located all five N atoms and one of the NCB groups. The function $\Sigma w(|F_o| - |F_c|)^2$ was minimized. Subsequent difference Fourier syntheses revealed all the atoms other than H. At this stage, using isotropic temperature factors for all 19 atoms, the discrepancy factors R_1 and R_2 were 0.101 and 0.110, respectively, where $R_1 = \Sigma||F_o| - |F_c||/\Sigma F_o$, $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o{}^2]^{1/2}$, and $w = 4F_o{}^2/\sigma^2(F_o{}^2)$.

In order to verify that the copper atom was bonded to the nitrogen of the $-NCBH_3$ groups and that no structural rearrangement had occurred which would result in the existence of $M-CNBH_3$ linkages (which has been proposed for $Fe(phen)_2(CNBH_3)_2$)[22] the least-squares refinement was rerun, assuming the compound was $(Me_5dien)Cu(CNBH_3)_2$ and varying the positional and isotropic thermal parameters of the cyanotrihydroborate carbon and nitrogen atoms. The temperature factors for the pseudo-nitrogen atoms decreased in value to 3.4 and 3.5 (from 5.9 and 5.8, respectively) while those for the pseudo-carbon atoms increased to 7.1 and 6.9 (from 5.2 and 4.9, respectively). In addition, the discrepancy factor R_1 increased somewhat from 0.101 to 0.106, and R_2 also increased slightly from 0.110 to 0.114. The original assumption that the compound is $(Me_5dien)Cu(NCBH_3)_2$ is therefore presumed to be correct.

Anisotropic temperature factors of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ were assigned to all

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(12) "International Tables for X-Ray Crystallography," Vol. I, 3rd ed, Kynoch Press, Birmingham, England, 1969, p 150.

(13) W. R. Busing, R. D. Ellison, H. A. Levy, S. P. King, and R. T. Roseberry, Report No. 4143, Oak Ridge National Laboratory, Oak Ridge, Tenn., Jan 1968.

(14) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 6, 197 (1967).

(15) "International Tables for X-Ray Crystallography," Vol. III, 3rd ed, Kynoch Press, Birmingham, England, 1969, p 162 ff.

(16) The calculation was performed using ORABS, a revised version of the Oak Ridge absorption correction program.

(17) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, 17, 1040 (1964).

(18) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42, 3275 (1965).

(19) D. T. Cromer, *Acta Crystallogr.*, 18, 17 (1965).

(20) A. J. C. Wilson, *Nature, (London)*, 150, 151 (1942). The program used was XDATA, the Brookhaven Wilson plot and scaling program.

(21) Calculations were performed on an IBM 360-91 computer using the following programs: FORDAP, the Zalkin Fourier program; CULS, the Columbia University version of the Busing–Martin–Levy structure factor calculation and least-squares refinement program, OR-FLS; ORFFE, the Busing–Martin–Levy molecular geometry and error function program; ORTEP, the Johnson thermal ellipsoid plotting program; and additional local data processing programs.

(22) D. F. Shriver, *J. Amer. Chem. Soc.*, 84, 4610 (1962); 85, 1405 (1963).

the atoms and the scattering factors for copper were corrected for both the real and the imaginary components of anomalous dispersion. A difference Fourier map following this refinement revealed the location of 23 of the 29 hydrogen atoms, and after these were refined isotropically the remaining 6 hydrogen atoms were located on a subsequent difference Fourier synthesis. During the last part of the refinement, it appeared that high negative $|F_o| - |F_c|$ values for several strong, low-order reflections could be due to the effect of uncorrected secondary extinctions. For this reason 5 reflections considered to be affected by extinction (021, 121, 102, 200, 210) were assigned zero weight in the last cycles.

The positional parameters and the isotropic temperature factors of the 29 hydrogen atoms, in addition to the positional parameters and the anisotropic temperature factors of the other 19 atoms, were refined in the last refinement cycles. No parameter varied by more than 0.1 of its estimated standard deviation, except for the three BH_3 hydrogen atoms on the apical $-NCBH_3$ group and one methyl hydrogen (H82), some of whose coordinates varied by 0.5 of their estimated standard deviations. The discrepancy indices converged at $R_1 = 0.031$ and $R_2 = 0.038$.

A final difference Fourier map showed only slight residual electron density of ~0.26 e/Å^3 near the BH_3 hydrogens whose positional parameters continued to vary slightly during the last refinement cycles and whose isotropic thermal parameters are rather large (see Table I). This may be due to a certain amount of disorder of the apical BH_3 group. The maximum height of the peaks on the final difference Fourier map was 0.1 the height of a carbon atom, as found in another difference Fourier map calculated without the contribution of that carbon atom.

In a test of the weighting scheme used, the function $w\Delta^2$ for the varying classes of reflections[23] was found to be approximately constant, and the structure was therefore considered to be complete.[24] The error on an observation of unit weight, $[\Sigma w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$, was 1.43.

Table I contains the final atomic positional and thermal parameters for all atoms, with their standard deviations derived from the inverse matrix of the last least-squares refinement cycle. Table II is a summary of the geometry of the molecule, and Table III lists the root-mean-square amplitudes of vibration for the atoms refined anisotropically. The sizes and orientations of the anistropic ellipsoids are shown along with the atom-labeling scheme in Figure 1.

Results and Discussion

Crystal and Molecular Structure. $(Me_5dien)Cu(NCBH_3)_2$ is a pentacoordinate complex of copper(II). Unlike the cyanotrihydroboratobis(triphenylphosphine)copper(I) complex,[1] this copper(II) compound exists as discrete monomeric molecular units in the solid state. The closest Cu-Cu approach is 7.997 Å as compared with 5.637 Å in the copper(I) cyanotrihydroborate bridged dimer[1] and 5.30 Å in the copper(I) thiocyanate bridged dimer.[25]. All intermolecular contacts are greater than the sum of the van der Waals radii of the atoms except for one C---C contact of 3.43 Å and two H---H contacts of 2.2 and 2.3 Å. Figure 2 shows how the molecules are packed in the unit cell. In contrast to bromoazido-1,1,7,7-tetraethyldiethylenetriamine-copper(II)[11] which has distorted trigonal-bipyramidal geometry, the coordination geometry of $(Me_5dien)Cu(NCBH_3)_2$ is that of a distorted square-based pyramid with one of the $-NCBH_3$ ligands occupying the apical position. Many authors have pointed out[26-28] that the various factors which determine the geometry of a pentacoordinate complex are usually so finely balanced that it is extremely difficult to explain the observed configuration. Considering only the effects of ligand-ligand repulsion,[29] a trigonal bipyramid

Table I. Final Positional and Thermal Parameters of the Atoms for $(Me_5dien)Cu(NCBH_3)_2$[a,b]

Atom	x	y	z	B, Å^2
Cu	0.21380 (3)	0.10799 (2)	0.13496 (3)	
N1	0.2790 (2)	0.1208 (2)	0.2583 (3)	
C1	0.2990 (2)	0.1352 (2)	0.3351 (3)	
B1	0.3209 (4)	0.1572 (3)	0.4403 (4)	
N2	0.1410 (2)	0.0097 (2)	0.1850 (2)	
C2	0.1080 (2)	−0.0442 (2)	0.2109 (3)	
B2	0.0608 (5)	−0.1206 (3)	0.2461 (5)	
N3	0.1299 (2)	0.1987 (2)	0.1671 (2)	
N4	0.1621 (2)	0.1156 (2)	−0.0002 (2)	
N5	0.3266 (2)	0.0615 (2)	0.0688 (2)	
C3	0.0713 (4)	0.2095 (3)	0.0834 (5)	
C4	0.1228 (4)	0.1927 (3)	−0.0073 (4)	
C5	0.2380 (3)	0.1043 (3)	−0.0676 (3)	
C6	0.2972 (3)	0.0430 (3)	−0.0296 (3)	
C7	0.1851 (4)	0.2679 (3)	0.1834 (4)	
C8	0.0746 (6)	0.1843 (3)	0.2544 (7)	
C9	0.0918 (4)	0.0578 (3)	−0.0195 (5)	
C10	0.3990 (4)	0.1192 (4)	0.0679 (5)	
C11	0.3594 (6)	−0.0077 (4)	0.1172 (5)	
H1	0.375 (2)	0.118 (2)	0.468 (3)	8 (1)
H2	0.258 (3)	0.149 (2)	0.478 (3)	8 (1)
H3	0.339 (2)	0.213 (2)	0.444 (2)	7 (1)
H4	0.051 (3)	−0.115 (3)	0.321 (4)	12 (2)
H5	0.101 (4)	−0.161 (3)	0.252 (4)	15 (2)
H6	0.005 (4)	−0.132 (3)	0.210 (4)	14 (2)
H31[c]	0.022 (3)	0.176 (2)	0.089 (3)	7 (1)
H32	0.054 (2)	0.259 (2)	0.085 (3)	7 (1)
H41	0.087 (2)	0.196 (2)	−0.062 (3)	7 (1)
H42	0.169 (3)	0.224 (2)	−0.014 (3)	7 (1)
H51	0.213 (2)	0.090 (2)	−0.134 (3)	8 (1)
H52	0.274 (2)	0.150 (2)	−0.070 (3)	6 (1)
H61	0.274 (3)	−0.013 (2)	−0.024 (3)	7 (1)
H62	0.349 (2)	0.035 (2)	−0.063 (2)	6 (1)
H71	0.145 (3)	0.309 (3)	0.194 (3)	11 (2)
H72	0.223 (3)	0.277 (3)	0.126 (3)	8 (1)
H73	0.224 (3)	0.258 (3)	0.240 (3)	8 (1)
H81	0.031 (3)	0.223 (3)	0.262 (3)	9 (1)
H82	0.112 (5)	0.170 (4)	0.300 (5)	16 (4)
H83	0.036 (3)	0.138 (3)	0.239 (3)	8 (1)
H91	0.061 (3)	0.064 (3)	−0.084 (3)	11 (1)
H92	0.118 (2)	0.006 (2)	−0.012 (2)	6.2 (9)
H93	0.048 (3)	0.064 (2)	0.018 (3)	6 (1)
H101	0.452 (3)	0.102 (2)	0.038 (3)	9 (1)
H102	0.413 (2)	0.129 (2)	0.135 (3)	6 (1)
H103	0.372 (3)	0.165 (3)	0.042 (3)	10 (2)
H111	0.305 (3)	−0.041 (3)	0.119 (4)	11 (2)
H112	0.375 (3)	0.007 (3)	0.179 (3)	10 (2)
H113	0.408 (3)	−0.029 (3)	0.081 (3)	11 (2)

Atom	β_{11}[d]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	5.77 (3)	3.28 (2)	5.94 (4)	−0.35 (2)	0.17 (2)	0.15 (2)
N1	9.7 (3)	5.6 (2)	6.7 (2)	−1.2 (2)	−0.6 (2)	−0.3 (2)
C1	6.5 (2)	4.0 (2)	7.2 (3)	−0.3 (1)	0.2 (2)	0.2 (2)
B1	8.1 (3)	3.9 (2)	7.0 (3)	0.5 (2)	−0.7 (3)	−0.0 (2)
N2	9.9 (2)	4.0 (1)	8.7 (2)	−1.6 (2)	0.7 (2)	1.0 (2)
C2	7.3 (2)	3.9 (2)	6.7 (3)	−0.6 (2)	−0.4 (2)	0.5 (2)
B2	9.8 (4)	4.5 (2)	9.1 (5)	−2.2 (3)	−0.8 (4)	2.5 (3)
N3	6.5 (2)	3.6 (1)	10.2 (3)	0.1 (1)	1.5 (2)	−0.2 (1)
N4	6.2 (2)	3.4 (1)	7.1 (2)	−0.9 (1)	−1.3 (2)	0.4 (1)
N5	6.2 (2)	4.6 (1)	7.5 (2)	0.4 (1)	0.1 (2)	0.1 (1)
C3	7.2 (3)	3.8 (2)	18.6 (7)	1.1 (2)	−0.9 (4)	−0.4 (3)
C4	9.7 (4)	4.2 (2)	11.6 (4)	−0.4 (2)	−4.5 (4)	1.2 (2)
C5	8.8 (3)	5.2 (2)	6.1 (3)	−1.3 (2)	−0.5 (2)	0.2 (2)
C6	8.2 (3)	5.7 (2)	7.6 (3)	−0.0 (2)	1.8 (3)	−0.9 (2)
C7	10.1 (4)	3.7 (2)	10.6 (4)	−0.3 (2)	0.8 (4)	−0.7 (2)
C8	11.3 (5)	4.9 (2)	17.2 (7)	0.3 (3)	7.8 (6)	−1.0 (3)
C9	7.6 (4)	4.5 (2)	11.3 (5)	−1.1 (2)	−2.6 (4)	0.2 (3)
C10	5.8 (3)	9.1 (3)	10.7 (5)	−0.4 (3)	−0.3 (3)	−1.1 (4)
C11	12.0 (5)	7.2 (3)	11.3 (5)	4.2 (4)	0.6 (5)	1.1 (3)

[a] Atoms are labeled as indicated in Figure 1. [b] Standard deviations, in parentheses, occur in the last significant figure for each parameter. [c] In this table H31, for example, refers to the first hydrogen on carbon atom 3. [d] β's are defined in the text; values reported here are $\times 10^3$.

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(23) D. W. J. Cruickshank in "Computing Methods of Crystallography," J. S. Rollett, Ed., Pergamon Press, New York, N. Y., 1965, pp 112-115.

(24) See paragraph at end of paper regarding supplementary material.

(25) A. P. Gaughan, R. F. Ziolo, and Z. Dori, *Inorg. Chim. Acta*, **4**, 640 (1970).

(26) L. Sacconi, *Pure Appl. Chem.*, **17**, 95 (1968).

(27) B. F. Hoskins and F. D. Whillans, *Coord. Chem. Rev.*, **9**, 365 (1973).

(28) P. L. Orioli, *Coord. Chem. Rev.*, **6**, 285 (1971).

(29) (a) J. Zemann, *Z. Anorg. Allg. Chem.*, **324**, 241 (1963); (b) D. L. Kepert, *Inorg. Chem.*, **12**, 1938 (1973).

Table II. Molecular Geometry of (Me$_5$dien)Cu(NCBH$_3$)$_2$[a]

Intramolecular Bond Distances, Å

(i) Coordination Sphere		(iii) The Triamine Ligand	
Cu-N1	1.980 (4)	N3-C3	1.464 (6)
Cu-N2	2.153 (3)	N4-C4	1.472 (5)
Cu-N3	2.069 (3)	N4-C5	1.474 (5)
Cu-N4	2.033 (3)	N5-C6	1.472 (5)
Cu-N5	2.069 (3)	N3-C7	1.484 (5)
		N3-C8	1.484 (6)
(ii) The -NCBH$_3$ Ligands		N4-C9	1.477 (5)
N1-C1	1.137 (5)	N5-C10	1.473 (6)
N2-C2	1.126 (4)	N5-C11	1.474 (6)
C1-B1	1.547 (6)	C3-C4	1.500 (7)
C2-B2	1.591 (6)	C5-C6	1.487 (6)
B1-H1	1.12 (4)	C3-H31	0.95 (4)
B1-H2	1.08 (4)	C3-H32	0.90 (4)
B1-H3	1.02 (3)	C4-H41	0.93 (4)
B2-H4	1.06 (5)	C4-H42	0.89 (4)
B2-H5	0.92 (6)	C5-H51	1.02 (4)
B2-H6	0.99 (5)	C5-H52	0.97 (4)
		C6-H61	1.05 (4)
		C6-H62	0.90 (3)

Selected Intramolecular Bond Angles, Deg

N1-Cu-N3	90.9 (1)	N1-Cu-N2	93.1 (1)
N1-Cu-N5	92.3 (1)	N3-Cu-N2	104.6 (1)
N3-Cu-N4	85.7 (1)	N4-Cu-N2	99.5 (1)
N4-Cu-N5	85.2 (1)	N5-Cu-N2	103.1 (1)
N3-Cu-N5	151.9 (1)	N1-Cu-N4	167.4 (1)
Cu-N1-C1	165.0 (3)	N1-C1-B1	176.7 (4)
Cu-N2-C2	175.6 (3)	N2-C2-B2	179.2 (8)
Cu-N3-C3	106.4 (3)	C3-N3-C7	109.8 (3)
Cu-N4-C4	105.6 (3)	C3-N3-C8	110.4 (3)
Cu-N4-C5	107.1 (2)	C4-N4-C5	112.2 (4)
Cu-N5-C6	105.4 (3)	C4-N4-C9	110.2 (3)
Cu-N3-C7	109.8 (2)	C5-N4-C9	109.0 (3)
Cu-N3-C8	112.0 (2)	C6-N5-C10	111.0 (3)
Cu-N4-C9	112.7 (2)	C6-N5-C11	109.7 (3)
Cu-N5-C10	108.3 (2)	C7-N3-C8	108.5 (2)
Cu-N5-C11	112.8 (2)	C10-N5-C11	109.6 (2)
N3-C3-C4	110.1 (4)	N4-C5-C6	108.5 (3)
C3-C4-N4	108.8 (4)	C5-C6-N5	110.0 (4)

[a] See footnotes *a* and *b*, Table I.

Table III. Root-Mean-Square Amplitudes of Vibration (Å)[a,b]

Atom	Min	Intermed	Max
Cu	0.2222 (8)	0.242 (2)	0.256 (1)
N1	0.251 (5)	0.287 (4)	0.341 (4)
C1	0.246 (5)	0.266 (5)	0.272 (5)
B1	0.245 (7)	0.259 (6)	0.305 (7)
N2	0.223 (5)	0.301 (4)	0.342 (4)
C2	0.238 (6)	0.257 (5)	0.293 (5)
B2	0.206 (7)	0.301 (8)	0.368 (8)
N3	0.237 (4)	0.257 (5)	0.327 (4)
N4	0.216 (4)	0.240 (4)	0.295 (4)
N5	0.252 (4)	0.269 (5)	0.278 (5)
C3	0.230 (6)	0.292 (6)	0.429 (7)
C4	0.240 (6)	0.263 (7)	0.399 (7)
C5	0.244 (6)	0.265 (6)	0.331 (6)
C6	0.244 (6)	0.298 (6)	0.325 (6)
C7	0.238 (6)	0.315 (7)	0.343 (7)
C8	0.237 (8)	0.286 (7)	0.48 (1)
C9	0.239 (7)	0.281 (7)	0.359 (8)
C10	0.251 (6)	0.318 (7)	0.383 (8)
C11	0.257 (7)	0.330 (8)	0.426 (9)

[a] Taken along the principal axes of the thermal ellipsoids. The orientation of these axes may be seen from Figure 1. [b] See footnotes *a* and *b*, Table I.

is more stable than a regular square pyramid if all five ligands are equivalent. However, a distorted square pyramid with the metal atom displaced from the basal plane toward the apical ligand is only slightly less stable than a trigonal bipyramid. In the calculated "most stable" square-pyramidal configuration,[29a] the apical atom-metal-basal atom bond angle is 104.1° and the basal atom-metal-basal atom bond angles are 86.6 and 151.9°. The geometry of (Me$_5$dien)Cu(NCBH$_3$)$_2$ is fairly close to this calculated "most stable" configuration. The four apical angles are not equal but are 104.6, 103.1, 99.5, and 93.1°. Note that the two larger angles are at N3 and N5, the terminal nitrogen atoms of the triamine ligand, each of which has two methyl group substituents. Thus the larger apical angles here are expected on the basis of steric considerations. The basal to basal bond angles are 85.2, 85.7, 90.9, 92.3, 151.9, and 167.4°. The two smallest angles are N3-Cu-N4 and N4-Cu-N5, which reflect the ligand "bite." The bite angle is 83.6° in bromoazidotetraethyldiethylenetriaminecopper(II)[11] and varies between 78.0 and 82.6° in Cu(dien)$_2$Br$_2$·H$_2$O[30] and Cu(dien)$_2$(NO$_3$)$_2$.[31] While ligand-ligand repulsions favor the trigonal-bipyramidal configuration, crystal field stabilization effects favor a regular square pyramid.[26,27] When the square pyramid is distorted so that the apical-metal-basal bond angle increases above 100°, the difference in crystal field stabilization energy between the two geometries is substantially reduced. With polydentate ligands, the steric restrictions imposed by the ligand geometry often determine, in the final analysis, the stereochemistry adopted by the complex.

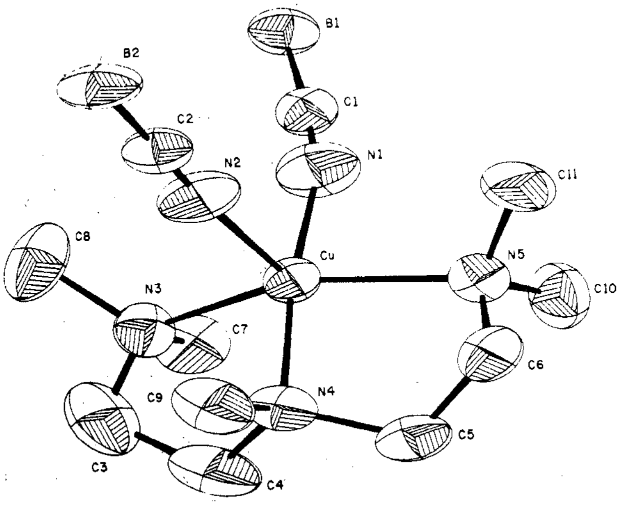

Figure 1. The structure of the molecule (Me$_5$dien)Cu(NCBH$_3$)$_2$ indicating the atom-labeling scheme. Hydrogen atoms are not shown. The 35% probability thermal ellipsoids are depicted.

The difference between the trigonal-bipyramidal structure of bromoazido-1,1,7,7-tetraethyldiethylenetriaminecopper(II) and the square-pyramidal structure of bis(cyanotrihydroborato)-1,1,4,7,7-pentamethyldiethylenetriamine copper(II) is somewhat analogous to the difference between the coordination geometries of Co(Et$_4$dien)Cl$_2$[9] and Co(Me$_5$dien)(Cl$_2$).[10] Co(Et$_4$dien)Cl$_2$ has a distorted trigonal-bipyramidal configuration while the geometry of Co(Me$_5$dien)Cl$_2$ cannot be easily described as either a distorted square pyramid or a distorted trigonal bipyramid; it has an intermediate geometry.[27,28] The nonbonded repulsions in the pentamethyl ligand appear to have forced the coordination polyhedron of cobalt in Co(Me$_5$dien)Cl$_2$ away from trigonal-bipyramidal toward square-pyramidal geometry.[28]

It has been noted[30] that the length of the Cu-N bond to the middle nitrogen atom of the triamine ligand is shorter than to the two terminal nitrogen atoms, and this is also found in both bromoazidotetraethyldiethylenetriamine-

(30) F. S. Stephens, *J. Chem. Soc. A*, 2233 (1969).
(31) F. S. Stephens, *J. Chem. Soc. A*, 883 (1969).

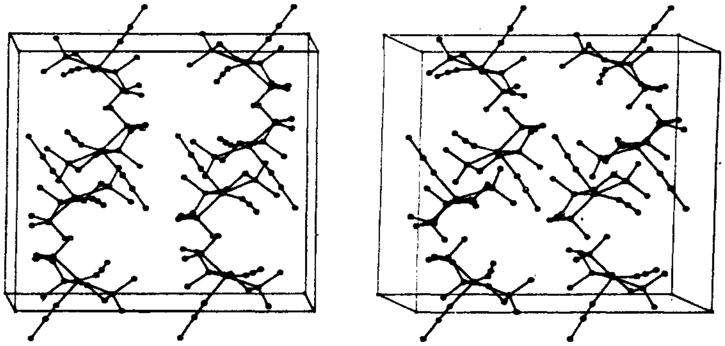

Figure 2. A stereoscopic view of one unit cell showing the packing of the eight molecules. The crystallographic *a* axis lies along the horizontal direction, the *b* axis is in the vertical direction, and the *c* axis completes a right-handed coordinate system.

copper(II) and $(Me_5dien)Cu(NCBH_3)_2$. The difference is considerably larger in the Et_4dien complex, however, where the middle nitrogen atom is apical and the other two are equatorial. The average Cu-N distance for the triamine ligand is shorter for the Me_5dien than for the Et_4dien complex. (Compare values given in Table II with those in ref 11.)

Bond distances and angles within the Me_5dien ligand itself appear normal. The nine N-C distances have a mean value of 1.475 (6) Å, the two C-C distances have a mean value of 1.494 (7) Å, and the maximum deviation from the tetrahedral angle about the N and C atoms is 4°.

The 23 methyl and methylene C-H distances have a mean value of 0.96 (5) Å with values ranging from 0.84 to 1.05 Å. These results agree with the recent conclusion[32] that the optimal X-ray C-H distance is 0.95 Å and that the refinement of positional and thermal parameters of hydrogen atoms can be a meaningful procedure and can lead to self-consistent results even in the presence of heavy atoms.

The four nitrogen atoms which form the "basal plane" of the square pyramid are not truly coplanar. If the plane of best fit for the four atoms N1, N3, N4, and N5 is calculated, it is found that two N atoms on opposite corners of the "square" lie above the plane, while the other two lie below the plane, with an average distance from the plane of 0.136 (20) Å. The copper atom lies 0.363 Å from this plane, displaced toward the apical N2 atom. The terminal nitrogen atoms of the triamine ligand, N3 and N5, are displaced away from the apical N2 atom. The dihedral angle through the planes defined by N3, N4, N5 and by N1, N3, N5 is 15.5°. A summary of the distances of other atoms from these planes is given in Table IV.

The Cu-N distances to the two cyanotrihydroborate ligands are strikingly different. The distance to the basal nitrogen atom, N1, is 1.980 (4) Å while the distance to the apical nitrogen atom, N2, is 2.153 (3) Å. These values should be compared to the average distance of 1.99 (3) Å found for $[((C_6H_5)_3P)_2Cu(NCBH_3)]_2$.[1] It is expected that the Cu-N distance in the basal (*xy*) plane will be shorter than the apical Cu-N distance for the following reason. With a square-pyramidal ligand field the $d_{x^2-y^2}$ orbital is highest in energy of the five 3d orbitals. Cu^{2+} has a d^9 configuration and therefore there is a single hole in the d shell, in the $d_{x^2-y^2}$ orbital. With a hole in the $d_{x^2-y^2}$ orbital the bonds in the *xy* plane will be relatively stronger than those along the apical *z* axis.

Table IV

Equations of Planes of Best Fit through the Basal N Atoms in Fractional Coordinates[a]

Plane	Atoms	Equation
1	N1, N3, N4, N5	$0.528x + 0.800y - 0.286z - 3.010 = 0$
2	N3, N4, N5	$0.468x + 0.788y - 0.400z - 2.723 = 0$
3	N1, N3, N5	$0.587x + 0.794y - 0.158z - 3.533 = 0$

Distances of Atoms from These Planes, Å

Plane 1	N1	−0.165 (3)	N3	0.133 (3)
	N4	−0.120 (3)	N5	0.124 (3)
	Cu*	−0.3625 (4)	N2*	−2.513 (3)
Plane 2	N1*	−0.560 (3)	N2*	−2.646 (3)
	Cu*	−0.5009 (4)		
Plane 3	N4*	−0.515 (3)	N2*	−2.586 (3)
	Cu*	−0.4713 (4)		

[a] Planes were weighted by the function $w_i = 3/[\sigma^2(x_i) + \sigma^2(y_i) + \sigma^2(z_i)]$. Atoms not used to define the plane are denoted by an asterisk.

There is also a difference of slightly more than 10° in the Cu-N-C bond angles for the two cyanotrihydroborate ligands. The Cu-N1-C1 angle is 165.0 (3)° which is comparable to the values of 160 (1) and 158 (1)° found for $[((C_6H_5)_3P)_2Cu(NCBH_3)]_2$,[1] 165 (4)° found for $Cu_2Cl_4(NCCH_3)_2$,[33] and 159 (1)° found for $Cu_3Cl_6(NCCH_3)_2$.[33] In most nitrile-metal complexes the linearity of the system M—N≡C—R is maintained and the deviation of the Cu-N-C angle from 180° in the examples mentioned above has been interpreted as an indication that the nitrogen atom does not use pure sp-hybrid orbitals, but orbitals with partial sp^2 character. The Cu-N2-C2 bond angle, however, is 175.6 (3)°. The large differences in Cu-N bond distances and Cu-N-C bond angles for the two $-NCBH_3$ ligands indicate a difference in bonding which is further evidenced by the appearance of two C-N stretching frequencies in the infrared spectrum, with an 18-cm^{-1} separation (*vide infra*).

The two N-C distances are 1.137 (5) Å for the basal $-NCBH_3$ ligand and 1.126 (4) Å for the apical ligand. These agree reasonably well with the average N-C bond distance of 1.14 (1) Å found in $[((C_6H_5)_3P)_2Cu(NCBH_3)]_2$,[1] 1.13 (2) Å reported for BF_3NCCH_3,[34] 1.17 and 1.134 Å found for $Cu_2Cl_4(NCCH_3)_2$ and $Cu_3Cl_6(NCCH_3)_2$, respectively,[33] and 1.17 (3) Å observed in the crystal of $VO(NO_3)_3 \cdot CH_3CN$, which contains the $NCCH_3$ ligand bonded through the N atom to the vanadyl ion.[35]

The mean C-B bond length in the $-NCBH_3$ ligands is 1.57 (2) Å which agrees well with the mean C-B bond length of 1.56 (3) Å reported for $[((C_6H_5)_3P)_2Cu(NCBH_3)]_2$.[1]

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(32) M. R. Churchill, *Inorg. Chem.*, 12, 1213 (1973).

(33) R. D. Willett and R. E. Rundle, *J. Chem. Phys.*, 40, 838 (1964).

(34) J. L. Hoard, T. B. Owen, A. Buzzell, and O. N. Salmon, *Acta Crystallogr.*, 3, 130 (1950).

(35) F. W. B. Epstein, E. Enwall, D. M. Morris, and D. Sutton, *Inorg. Chem.*, 10, 678 (1971).

The average B-H distance for the basal $-NCBH_3$ ligand is 1.07 (4) Å which is slightly shorter than the 1.125 Å average value reported for the copper(I)-bridged dimer.[1] The very short values found for the apical boron-hydrogen bond distances are not considered to be significant because two of these H atoms (H5 and H6) refined away from the positions at which they were located on the Fourier map and it is in that vicinity that some small residual electron density appears on the final difference Fourier.

Table V compares intramolecular bond distances within the $-NCBH_3$ ligands for the two compounds $(Me_5dien)Cu(NCBH_3)_2$ and $[((C_6H_5)_3P)_2Cu(NCBH_3)]_2$. Note that in each case the shorter Cu-N distance is associated with the longer N-C distance and the shorter C-B distance. While it is recognized that statistically there is no significant difference in the four N-C bond distances listed in Table V, these results seem to indicate that a stronger, shorter bond between copper and the nitrogen atom of the ligand leads to a slight increase in the C≡N bond distance and a corresponding shorter, stronger bond between the carbon and boron atoms.

Infrared Spectrum. The infrared spectrum of a Nujol mull of solid $(Me_5dien)Cu(NCBH_3)_2$ shows two strong bands in the C≡N stretching region, one at 2192 cm^{-1} and one at 2210 cm^{-1}. These are both at higher frequency than the C≡N stretch in KBH_3CN which occurs at 2179 cm^{-1}.[36] It is well known that coordination of nitriles causes a shift of the C≡N stretch to higher frequencies.[37-40] This has been explained in terms of a rehybridization of the N orbitals on coordination which leads to an increase in the C≡N force constant.[39,41,42] In the uncomplexed anion the lone pair of electrons on the nitrogen atom has more "s" character than a pure sp hybrid and therefore the N-C σ bond has less "s" character than does a pure sp hybrid. On coordination, if a linear M-N-C-R configuration is formed, nitrogen uses pure sp orbitals to bond to both the metal and the carbon atoms. The C-N σ bond thus acquires more "s" character and is both strengthened and shortened, shifting the C≡N stretching frequency to higher energy. Indeed, the shift of the stretching frequency to higher values in the spectra of complexes of nitriles has been cited as good evidence for linear M-N-C-R bonds.[43] Decreasing the M-N-C bond angle significantly from 180°, however, requires some sp^2 character in the hybrid orbitals used by nitrogen for σ bonding to carbon.

In the case of the two $-NCBH_3$ groups in $(Me_5dien)Cu(NCBH_3)_2$ it is noted that the basal ligand has the stronger Cu-N bond, but the longer N-C bond (see Table V) and a Cu-N1-C1 bond angle of 165°, while the apical ligand has a weaker, significantly longer (2.153 (3) Å) Cu-N bond, but the shorter N-C bond distance and a Cu-N-C bond angle of 175.6°. We conclude, therefore, that the higher frequency, 2210 cm^{-1}, corresponds to the C≡N stretch in the apical ligand, while the lower frequency, 2192 cm^{-1}, corresponds to the basal ligand C≡N stretch.

Table V. Comparison of Intramolecular Distances (Å) for the Cu-$NCBH_3$ groups in $(Me_5dien)Cu(NCBH_3)_2$ and $[((C_6H_5)_3P)_2Cu(NCBH_3)]_2$

Compd	Cu-N	N-C	C-B	Ref
$[((C_6H_5)_3P)_2Cu(NCBH_3)]_2$	1.96 (1)	1.15 (1)	1.53 (2)	1
$(Me_5dien)Cu(NCBH_3)_2$	1.980 (4)	1.137 (5)	1.547 (6)	This work
$[((C_6H_5)_3P)_2Cu(NCBH_3)]_2$	2.01 (1)	1.13 (1)	1.59 (2)	1
$(Me_5dien)Cu(NCBH_3)_2$	2.153 (3)	1.126 (4)	1.591 (6)	This work

It is useful to summarize the infrared spectral differences between the $-NCBH_3$ group as a bridging ligand and as a terminal, monodentate ligand. (1) The terminal B-H stretching mode ($\nu^{e}{}_{BH}$) in $(Me_5dien)Cu(NCBH_3)_2$ consists of a strong broad band with a maximum at 2346 cm^{-1} and shoulders at 2396 and 2284 cm^{-1}. In $[(C_6H_5)_3P]_3Cu(NCBH_3)$, another complex with a monodentate ligand, this band is centered at 2330 cm^{-1}.[6] In the dimeric cyanotrihydroborate-bridged structure[6] this band is shifted to higher frequency and occurs at 2376 cm^{-1}. (2) The two terminal H-B-H deformation modes ($\delta^{a_1}{}_{BH}$) occur as two strong sharp peaks at 1123 and 1112 cm^{-1} in $(Me_5dien)Cu(NCBH_3)_2$. In the dimeric $[((C_6H_5)_3P)_2Cu(NCBH_3)]_2$ this H-B-H bending mode is shifted to lower frequency, *ca.* 1100 cm^{-1}.[6] (3) In the dimer there is a broad underlying band at ~2200 cm^{-1} due to a Cu-H-B stretching vibration which is absent in the two monodentate complexes.

Electrical Conductivity. The molar conductivities of 1.0×10^{-3} *M* solutions of $(Me_5dien)Cu(NCBH_3)_2$ in both methanol and water at 25° are indicative of a 1:1 electrolyte. Values of the molar conductance in methanol varied from 66.4 ohm^{-1} cm^2 mol^{-1} at 15.3×10^{-4} *M* to 88.9 ohm^{-1} cm^2 mol^{-1} at 3.79×10^{-4} *M*. Literature values of the molar conductances of a large number of 1:1 electrolytes in methanol at these concentrations range from 70 to 115 ohm^{-1} cm^2 mol^{-1}.[44-48] We interpret these values as being due to almost complete dissociation of the apical $-NCBH_3$ ligand since the structural studies show that this group is less tightly bound to the copper than is the basal cyanotrihydroborate ligand. A plot of Λ_M *vs.* the square root of the concentration for these methanol solutions of $(Me_5dien)Cu(NCBH_3)_2$, however, is not linear but has a slope which increases more steeply as the concentration is decreased, which is characteristic behavior for a weak electrolyte. The molar conductivities of $[(C_6H_5)_3P]_3Cu(NCBH_3)$, $[((C_6H_5)_3P)_2Cu(NCBH_3)]_2$, and $((C_6H_5)_3P)_2Cu(B_3H_8)$ in acetonitrile also exhibit this type of behavior.[6] We suggest, therefore, that the cation formed after dissociation of the apical ligand behaves as a weak electrolyte and that an equilibrium exists in solution between dissociated and undissociated forms involving the basal $-NCBH_3$ ligand.

The molar conductance of 1.0×10^{-3} *M* $(Me_5dien)Cu(NCBH_3)_2$ in water at 25° is 154 ohm^{-1} cm^2 mol^{-1} which is a little larger than typical values for 1:1 strong electrolytes. It has been observed[36] that aqueous solutions of $NaBH_3CN$ are basic due to the equilibrium $BH_3CN^- + H_2O = BH_3CNH$

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(36) J. R. Berschied, Jr., and K. F. Purcell, *Inorg. Chem.*, **9**, 624 (1970).

(37) H. J. Coerver and C. Curran, *J. Amer. Chem. Soc.*, **80**, 3522 (1958).

(38) R. A. Walton, *Quart. Rev., Chem. Soc.*, **19**, 126 (1965).

(39) J. C. Evans and G. Y-S. Lo, *Spectrochim. Acta*, **21**, 1033 (1965).

(40) J. Reedijk, A. P. Zuur, and W. L. Groeneveld, *Recl. Trav. Chim. Pays-Bas*, **86**, 1127 (1967).

(41) K. F. Purcell and R. S. Drago, *J. Amer. Chem. Soc.*, **88**, 919 (1966).

(42) K. F. Purcell, *J. Amer. Chem. Soc.*, **89**, 267, 6139 (1967).

(43) M. Kubota and D. L. Johnston, *J. Inorg. Nucl. Chem.*, **29**, 769 (1967).

(44) E. C. Evers and A. G. Knox, *J. Amer. Chem. Soc.*, **73**, 1739 (1951).

(45) R. E. Jervis, D. R. Muir, J. P. Butler, and A. R. Gordon, *J. Amer. Chem. Soc.*, **75**, 2855 (1953).

(46) P. G. Sears, R. R. Holmes, and L. R. Dawson, *J. Electrochem. Soc.*, **102**, 145 (1955).

(47) P. G. Sears, R. L. McNeer, and L. R. Dawson, *J. Electrochem. Soc.*, **102**, 269 (1955).

(48) D. A. MacInnes, "The Principles of Electrochemistry," Dover Publications, New York, N. Y., 1961, pp 357-358.

+ OH^- for which $K_b = 2 \times 10^{-10}$. The presence of the highly mobile hydroxide ion will of course increase the conductivity. A plot of Λ_M *vs.* the square root of the concentration for the aqueous solutions also rises more steeply with dilution than is expected for a 1:1 strong electrolyte. Dissociation of the cyanotrihydroborate ligands in both water and methanol, therefore, appears to involve similar processes.

Conductivity measurements were also carried out in nitromethane. The compound decomposes in CH_3NO_2; in a fairly short time the color of the solution changes from deep royal blue to a light blue-green. The conductivity of a 1.0×10^{-3} *M* solution in nitromethane is initially quite low ($\Lambda_M \approx 14$ ohm^{-1} cm^2 mol^{-1}) but it increases fairly rapidly with time. After 21.5 hr $\Lambda_M = 29.2$ ohm^{-1} cm^2 mol^{-1}.

Magnetic Susceptibilty. The gram magnetic susceptibility was measured as a function of temperature over the range 80-300°K by the Faraday method.[49] The calibrant used was $HgCo(SCN)_4$. The temperature calibration of the cryostat was checked by calculating the magnet constant[49] β at a series of temperatures. The values of β measured on our equipment for three different field strengths over the temperature range 80-350°K were constant to within 1-2%. The molar magnetic susceptibility was corrected for diamagnetic substituents using Pascal's constants[50] and also for temperature-independent paramagnetism.[51] The diamagnetic correction term is -176×10^{-6}. Since the visible spectrum of $(Me_5dien)Cu(NCBH_3)_2$ in methanol solution consists of one single broad peak with λ_{max} 6450 Å, the correction term for temperature-independent paramagnetism is $\chi_{TIP} = 1.04/\Delta = (1.04)(6.45 \times 10^{-5}) = 67 \times 10^{-6}$.[51]

The effective magnetic moment, in Bohr magnetons, was obtained from the corrected molar magnetic susceptibility using the relation $\mu_{eff} = 2.83(\chi_M^{cor}T)^{1/2}$ where T is the absolute temperature. The value of the effective magnetic moment of $(Me_5dien)Cu(NCBH_3)_2$ was 1.79 ± 0.02 BM throughout the temperature range 80-300°K. This is just slightly above the "spin-only" value of 1.73 BM and is typical of a monomeric molecular copper(II) compound.

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Registry No. $(Me_5dien)Cu(NCBH_3)_2$, 50276-24-9.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-822.

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(49) L. F. Lindoy, V. Katovic, and D. H. Busch, *J. Chem. Educ.*, 49, 117 (1972).

(50) W. L. Jolly, "The Synthesis and Characterization of Inorganic Compounds," Prentice-Hall, Englewood Cliffs, N. J., 1970, p 371.

(51) W. L. Jolly, ref 50, p 378.

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Synthesis and Properties of Cationic Molybdenum(IV) Oxohaloisocyanide Complexes

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The reactivity of binary molybdenum chlorides toward isocyanide ligands in the presence of oxygen-containing solvents has been investigated under an atmosphere of dry nitrogen. If ether is used as the solvent, the known seven-coordinate $[Mo(CNR)_7]X_2$ compounds are formed. When methanol is used as the solvent, new oxo species of the type $[(RNC)_4MoOCl]Y$ can be prepared. These latter complexes are characterized by infrared, pmr, and optical spectroscopy and by solution conductivity studies in nitromethane. The trans isomer predominates. The synthesis of the oxobromo analog, $[(CH_3NC)_4MoOBr]^+$, from molybdenum hexacarbonyl is described.

Introduction

The present study grew out of a program to prepare and characterize eight-coordinate MX_4Y_4 complexes containing only monodentate ligands.[1] In particular, we were interested in carrying out reaction 1 with various R groups and

$$MoX_4 + 4RNC \rightarrow Mo(CNR)_4X_4 \qquad (1)$$

halides and structurally characterizing the products. The chemistry represented by eq 1 has not yet been observed, however, because of the tendency for anhydrous metal halides to abstract oxygen from solvent molecules[2] or to be reduced by isocyanide ligands.[3] As described in this report, several new examples of the relatively rare molybdenum(IV)-oxo species,[4,5] as well as the known heptacoordinate molybdenum(II) isocyanide cation,[6] were isolated.

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(1) M. Novotny, D. F. Lewis, and S. J. Lippard, *J. Amer. Chem. Soc.*, 94, 6961 (1972), and references cited therein.

(2) R. A. Walton, *Progr. Inorg. Chem.*, 16, 1 (1972).

(3) L. Malatesta and F. Bonati, "Isocyanide Complexes of Metals," Wiley-Interscience, New York, N. Y., 1969.

(4) (a) S. J. Lippard and B. J. Russ, *Inorg. Chem.*, 6, 1943 (1967); (b) J. Van de Poel and H. M. Neumann, *ibid.*, 7, 2086 (1968); (c) V. W. Day and J. L. Hoard, *J. Amer. Chem. Soc.*, 90, 3374 (1968).

(5) (a) D. Grdenic and B. Korpar-Colig, *Proc. Chem. Soc., London*, 308 (1963); (b) R. N. Jowitt and P. C. H. Mitchell, *J. Chem. Soc. A*, 2632 (1969); (c) A. V. Butcher and J. Chatt, *ibid.*, 2652 (1970); (d) L. K. Atkinson, A. H. Mawby, and D. C. Smith, *Chem. Commun.*, 1399 (1970), and references cited therein.

(6) M. Novotny and S. J. Lippard, *J. Chem. Soc., Chem. Commun.*, 202 (1973).