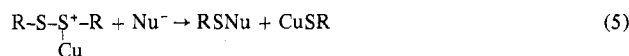


Figure 3. Stereoview of the structure, illustrating the packing of the ions within the unit cell. Ellipsoids of 15% probability are used.



sulfur bond.²⁹ Such a mechanism could explain the susceptibility of the [CuL]₂²⁺ complex to decomposition in boiling methanol (see Characterization of Complexes). A similar intermediate disulfide complex has been isolated in the palladium chloride assisted scission of the disulfide bond in diphenyl disulfide.⁹

The mean sulfur-carbon bond length is 1.83 (2) Å. It has not been very precisely determined, but it appears to be normal.⁸ Other features of the molecular geometry, as given in Table IV, are not unusual. The tetrafluoroborate groups are normal except for one B-F distance, which is quite short but insignificantly so. The large standard deviations in the bonds and angles involving boron, carbon, and nitrogen make a further detailed discussion of these values inappropriate. The arrangement of the ions in the crystal is indicated in Figure 3.⁶⁶

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Registry No. [CuL]₂(BF₄)₂, 51065-42-0; [CuL]₂(ClO₄)₂, 51153-48-1.

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-74-1904.

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X-Ray Structural Characterization of an Outer-Sphere Copper(II) Dimer, [Cu₂(tren)₂(CN)₂](BPh₄)₂. Hydrogen Bonding between Two Trigonal-Bipyramidal Copper Cations

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The structure of [Cu₂(tren)₂(CN)₂](BPh₄)₂, the tetraphenylborate salt of an outer-sphere dimer of cyano-2,2',2''-tri-aminotriethylaminecopper(II) cation, where tren = 2,2',2''-tri-aminotriethylamine, has been determined using heavy-atom least-squares X-ray methods to conventional observed-calculated agreement factors of $R_F = 0.067$ and $R_{wF} = 0.047$ for 2773 reflections measured on a four-circle diffractometer. The molecule crystallizes in the $P2_1/c$ space group with two formula weights in a cell measuring $a = 13.792$ (7) Å, $b = 10.338$ (6) Å, $c = 20.316$ (14) Å, and $\beta = 94.27^\circ$ (4). The crystal densities are 1.26 (calculated) and 1.27 g/cm³ (measured). Discrete cationic [Cu₂(tren)₂(CN)₂]²⁺ and anionic BPh₄⁻ units are found. Each copper atom in the cation is trigonal bipyramidally coordinated with tren occupying four sites [Cu-N = 2.076 (5), 2.090 (5), 2.119 (5), and 2.083 (5) Å] and with an axial carbon-bonded cyanide [Cu-CN = 1.967 (7) Å and C-N = 1.127 (9) Å]. The trigonal bipyramids are distorted from perfect threefold symmetry with trigonal-plane angles of 122.6 (2), 120.4 (2), and 112.5 (2)°. The cation is dimeric by virtue of the fact that the coordinated cyanide on each copper atom is hydrogen bonding through its nitrogen atom to a primary amine of the tren ligand coordinated to the second copper atom, *i.e.*, Cu-CN...HN-Cu. The N-N distance across the hydrogen bond is 3.047 (7) Å. The dimeric cation is located on a center of inversion in the unit cell and the Cu-Cu distance is 6.090 (1) Å. The angle between the two copper pseudotrigonal axes (each defined as being collinear with the Cu-C bond) and the Cu-Cu vector is 44°. The conformation and inter-ring interactions of the BPh₄⁻ anion are discussed.

Introduction

Several reviews³⁻⁷ have appeared in part or in total con-

cerned with transition metal cyanide complexes. The bridging nature of the cyanide ion has been well documented and, in fact, this aspect of the interaction of cyanide with transition metals has been the focal point of two^{5,6} of the above reviews. The best known systems with bridging cy-

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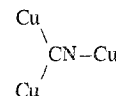
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nide are the Prussian blue system and its many analogs. A very recent review⁷ has summarized the structural chemistry of these three-dimensional polymeric cyanides (as well as other polymeric cyanides) possessing end-to-end cyanide bridging.

Various physical techniques have been used to implicate end-to-end cyanide bridging in transition metal dimers and clusters. Diethyl- and di-n-propylgold cyanides are known⁸ to be tetrameric by cryoscopy and on the basis of a preliminary X-ray study⁹ were indicated to have end-to-end cyanide bridging between four gold atoms arranged in a square. A similar structure was proposed¹⁰ for $\text{Pd}(\text{CN})_2 \cdot \text{NH}_3$. End-to-end cyanide bridging has also been indicated in various anions such as $[(\text{NC})_5\text{Fe}-\text{CN}-\text{Co}(\text{CN})_5]^{6-}$ ¹¹ and $[(\text{NC})_3(\text{O})_2-\text{CN}-\text{Re}(\text{O})(\text{CN})_4]^{6-}$ ¹² and in cations such as that found in $[(\text{A})\text{Cu}-\text{CN}-\text{Cu}(\text{A})](\text{ClO}_4)_3$ ¹³ where A = hexamethyltetraazacyclotetradecadiene. The basicity of the nitrogen end of a coordinated cyanide has been demonstrated^{14,15} by adduct formation with BX_3 to give materials such as $\text{K}_2\text{Ni}(\text{CN} \cdot \text{BF}_3)_4$. The importance of characterizing this end-to-end bridging of cyanide is gauged by the amount of recent work on the viability of cyanide as an electron-transfer bridge¹⁶⁻¹⁸ between two redox centers and on the effect¹⁹⁻²¹ cyanide has on certain cuproproteins. With respect to end-to-end cyanide bridging in transition metal dimers and clusters, it is important to note that the only single-crystal X-ray work on such a system was recently reported²² for $(\text{NC})_5\text{Co}-\text{CN}-\text{Co}(\text{NH}_3)_5 \cdot \text{H}_2\text{O}$, which was prepared in 1969 by Haim and coworkers.²³

Cyanide bridging in copper compounds has not been as well studied, for copper(II) this is a reflection of the fact that Cu(II) is reduced to Cu(I) in the presence of cyanide.²⁴ Cromer and coworkers have determined the structures of a series of polymeric copper(I) cyanide complexes: $\text{KCu}(\text{CN})_2$,²⁵ $\text{KCu}_2(\text{CN})_3 \cdot \text{H}_2\text{O}$,²⁶ $\text{CuCN} \cdot \text{N}_2\text{H}_4$,²⁷ and $\text{CuCN} \cdot \text{NH}_3$.²⁸ In the case of the first three polymers Cu-CN-Cu

bridging is present, whereas the last polymer displays a cyanide bridging with a bifurcated carbon atom



The first stable copper(II) cyanide was reported in 1966¹³ and more recently end-to-end cyanide bridging was demonstrated by X-ray techniques²⁹ for the polymeric mixed-valence compound, $\text{Cu}_3(\text{NH}_3)_3(\text{CN})_4$.

We very recently prepared a compound which variable-temperature magnetic susceptibility³⁰ showed to possess an antiferromagnetic exchange interaction and which we consequently formulated as a dimer, $[\text{Cu}_2(\text{tren})_2(\text{CN})_2](\text{BPh}_4)_2$, where tren is 2,2',2''-tri-aminotriethylamine. In view of preliminary epr studies which indicated the copper coordination to be trigonal bipyramidal, it was thought that the mode of bridging in this complex would best be discovered by X-ray techniques. In the present paper the results of a single-crystal X-ray diffraction study of this compound are presented. The antiferromagnetic exchange interaction between the two copper atoms in the dimer will be shown to be a result of an unusual type of end-to-end cyanide bridging.

Experimental

Compound Preparation. In our preparation of $[\text{Cu}_2(\text{tren})_2(\text{CN})_2](\text{BPh}_4)_2$ 0.01 mol of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was dissolved in distilled water, ~1.5 ml of tren (triethylenetetramine) was added, and into this solution was stirred 0.01 mol of NaCN dissolved in water. A water solution of NaBPh_4 was then added resulting in the immediate precipitation of a blue powder. The quantity of NaBPh_4 added was much less than stoichiometric (10-20% of the calculated amount). The apparent disparity between the starting materials (tren) and products (tren) of this reaction lies in the use of tren (Aldrich) which is in fact 10-20% tren! Apparently, tren product is the least soluble BPh_4^- salt. Analytically there is no way to differentiate between the tren and tren products; however, a comparison of ir data with authentic tren complexes made from pure tren shows that the powder we obtain is a tren compound. This was, of course, confirmed by the crystallographic results herein reported.

Crystals of $[\text{Cu}_2(\text{tren})_2(\text{CN})_2](\text{BPh}_4)_2$ were obtained by slow evaporation of an acetonitrile solution of the blue powder. Two crystal habits were observed: one is a parallelepiped and the second is best described as a six-sided plate. Powder pattern studies indicated that the two systems have the same structure and precession photography on both crystalline types established the equivalence of unit cell dimensions, space group ($P2_1/c$) and relative intensities. It was also found that the powder patterns of the precipitated powder and ground crystalline material were identical.

Crystal Measurements. Studies were carried out using a computer-controlled Picker FACS-1 X-ray diffractometer system with the crystal mounted in a four-circle goniostat. Molybdenum $K\alpha$ radiation was used, monochromated by a graphite crystal at a takeoff angle of 1.55° .

The crystal of $[\text{Cu}_2(\text{tren})_2(\text{CN})_2](\text{BPh}_4)_2$ used for this study was of the six-sided type. It was 0.08 mm thick and had distances between pairs of opposite edges of 0.50, 0.50, and 0.42 mm. As indicated above, precession photography established the space group as $P2_1/c$. Reflection data were collected with the crystal rotating about an axis normal to a six-sided face, this axis corresponding to the a^* axis of the reciprocal cell. Centering of 13 reflections ($2\theta = 24-31^\circ$) by hand allowed refinement of the unit cell parameters to their final values of $a = 13.792$ (7) Å, $b = 10.338$ (6) Å, $c = 20.316$ (14) Å, and $\beta = 94.27$ (4) $^\circ$. Using these parameters and mol wt 1091.9 ($Z = 2$ dimers) leads to the density $\rho_{\text{calcd}} = 1.26$ g/cm³ whereas ρ_{obsd} (toluene-bromotoluene flotation) = 1.27 g/cm³.

For the data collection the base width of the scans was set at 2.1° in 2θ ($\theta-2\theta$ scan technique used) and dispersion corrections were made to compensate for $K\alpha_1$, $K\alpha_2$ splitting for high 2θ reflections. Scans were made at 1° min^{-1} of all unique reflections from $2\theta = 4^\circ$

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to $2\theta = 40^\circ$. Three standard reflections were measured every 50 reflections and realignment was made as was necessary to keep the intensities of these reflections above 95% of their maximum values. Backgrounds were counted for 10 sec on each side of a peak. A total of 2773 unique reflections were collected, of which 2199 were observed ($I_{\text{obsd}} > 2\sigma(I)$ where $\sigma(I) = [T_c + (t_c/t_b)^2(B_1 + B_2)]^{1/2}$; T_c is the total integrated peak count, t_c/t_b is the ratio of time spent counting the peak intensity to the time of counting the background intensities, and B_1 and B_2 are the background counts). Lorentz and polarization corrections were made. Anomalous dispersion corrections were made for the copper atoms only.

Structure Solution and Refinement. Generation of a Fourier map from the copper atom position obtained from a Patterson function calculation (the spherical atom scattering factors used in this and following calculations were reported by Hansen, *et al.*,³¹ for Cu, N, B, and H and by Cromer and Mann³² for C) led to the location of 24 additional atoms. Treating these 24 atoms as carbon atoms (they were not assignable at this stage), a second Fourier map was calculated and from this all cation and tetraphenylborate atoms were identified. With all Cu, C, and N atoms included, three cycles of isotropic refinement using the computer program ORFLS (written by Busing and Levy) were calculated. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/(\sigma(F))^2$ and $\sigma(F) = (|F|/2I)[T_c + (t_c/t_b)^2(B_1 + B_2) + (0.03I)^2]^{1/2}$. The conventional unweighted and weighted agreement factors were $R_F = 0.146$ ($R_F = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$) and $R_{wF} = 0.213$ ($R_{wF} = (\Sigma w|F_o - F_c|^2/\Sigma wF_o^2)^{1/2}$) and the refinement had converged at this point. Although the R factors were unacceptably high at this point, one cycle of anisotropic refinement was run (in two parts, first varying the copper cation atoms and then those of the tetraphenylborate; this was done because of the computer program capacity of 270 parameters). This anisotropic run lowered the R factors to $R_F = 0.149$ and $R_{wF} = 0.197$. It was noticed at this time that ~ 100 reflections were observed to be much weaker than their calculated values; two steps were taken to improve the fit before remeasurement of these ~ 100 reflections was deemed necessary. First, an absorption correction was made (using a locally modified version of ORABS³³) where the maximum and minimum transmission factors were 0.80 and 0.69. Second, the statistical weighting scheme in use was weighting the weaker reflections more and the stronger reflections less than was appropriate from analysis of $|F_o - F_c|$ as a function of F_o (this is why R_{wF} was so much larger than R_F) so the following scheme was used: if $F_o < 4F_{\text{min}}$, then $\sigma(F) = 1.0 + 4F_{\text{min}}/F_o$ or if $F_o < 4F_{\text{min}}$, then $\sigma(F) = 1.0 + 0.1F_o/4F_{\text{min}}$; F_{min} was taken as 8.0. This is a modification of Hughes' scheme.³⁴ With the observed-unobserved cutoff being 3σ there were 2314 observed reflections.

At this point two cycles of isotropic least-squares calculations were performed resulting in $R_F = 0.134$ and $R_{wF} = 0.146$. The positions of all hydrogen atoms were then calculated. Three complete cycles of anisotropic refinement (now with hydrogen atoms) gave $R_F = 0.114$ and $R_{wF} = 0.121$.

It was the remaining disagreement for many structure factors and the unreasonableness of one bond length (C2-N2 = 1.33 Å) which dictated the recollection of 97 reflections. Standard reflections were chosen upon which to base the scaling of the remeasured data into the original data set. Standards were chosen to be of convenient size ($45 < F_o < 150$) which show good agreement with the F_c values. Data were recollected on the same crystal and mounting as used originally. Before measuring the 97 reflections, 8 standards were measured and then 14 more standards were measured after data collection. The scaling factor required to scale the F_o (corrected for Lorentz and polarization effects) obtained for the standards to those for the original data set was 1.136 with a standard deviation (all 22 standards) of 0.036. The two sets of standards showed essentially the same average deviation from the values previously measured. Calculating F_o for all 97 reflections, scaling, and merging into the original data set led, after two complete cycles of anisotropic least-squares (with hydrogen atoms positioned as calculated with N-H and C-H distances of 0.95 Å with temperature factors set equal to those found

Table I. Positional Parameters for Dimer Atoms^a

Atom	x/a	y/b	z/c
Cu	0.16457 (5)	0.07599 (7)	0.10080 (3)
N1	0.2572 (3)	0.2338 (5)	0.1133 (2)
N2	0.2765 (4)	0.0030 (5)	0.0477 (2)
N3	0.1946 (4)	0.0577 (6)	0.2042 (2)
N4	0.0665 (3)	0.2148 (5)	0.0624 (2)
N5	0.0234 (4)	-0.1542 (6)	0.0757 (3)
C1	0.3375 (5)	0.2175 (6)	0.0686 (3)
C2	0.3636 (4)	0.0775 (7)	0.0657 (3)
C3	0.2957 (5)	0.2369 (7)	0.1835 (4)
C4	0.2218 (5)	0.1876 (8)	0.2274 (3)
C5	0.2000 (5)	0.3504 (6)	0.0958 (4)
C6	0.1230 (5)	0.3245 (6)	0.0424 (3)
C7	0.0741 (4)	-0.0700 (7)	0.0863 (3)

^a Standard deviations of the least significant digits are in parentheses. The hydrogen atom positions were computed geometrically based upon positions of the tren atoms.

Table II. Temperature Factors^a and Estimated Standard Deviations for the [Cu₂(tren)₂(CN)₂]²⁺ Cation ($\times 10^4$)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	53.4 (4)	95.5 (8)	24.6 (2)	-6.9 (6)	0.7 (2)	-1.8 (5)
N1	72 (4)	82 (6)	33 (2)	-2 (4)	-1 (2)	-1 (3)
N2	70 (3)	111 (6)	29 (2)	-10 (4)	5 (2)	2 (3)
N3	88 (4)	186 (9)	22 (1)	-16 (5)	2 (2)	6 (3)
N4	67 (4)	141 (7)	32 (2)	10 (4)	-5 (2)	-6 (3)
N5	69 (4)	147 (8)	42 (2)	-41 (5)	8 (2)	-10 (3)
C1	76 (5)	102 (9)	39 (2)	-23 (5)	7 (3)	7 (4)
C2	54 (4)	147 (9)	27 (2)	10 (6)	5 (2)	-2 (4)
C3	82 (5)	129 (9)	39 (3)	-8 (6)	-12 (3)	-26 (4)
C4	84 (5)	199 (12)	24 (2)	29 (7)	1 (3)	-20 (4)
C5	103 (6)	86 (8)	51 (3)	4 (6)	4 (4)	4 (4)
C6	98 (6)	93 (9)	38 (2)	15 (6)	8 (3)	18 (4)
C7	48 (4)	128 (9)	26 (2)	1 (6)	8 (2)	5 (4)

^a The form of the anisotropic thermal ellipsoid is given by $B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl$.

for the connected carbon or nitrogen atom after isotropic refinement, the range in B being 3.35 – 7.02 Å²) to reduction of the agreement factors to $R_F = 0.060$ and $R_{wF} = 0.052$. The unobserved data were added to give a total of 2773 reflections and then two more complete cycles of anisotropic refinement with all atoms resulted in a final fit of $R_F = 0.067$ and $R_{wF} = 0.047$, and the ERF (expected error in a measurement of unit weight) was 1.808. A final difference Fourier shows a peak of 0.45 e/Å³ near the metal atom; there are no other peaks larger than 0.25 e/Å³. During the last cycle of fitting no parameter changed by as much as half its estimated standard deviation.

The final values of $|F_o|$ and $|F_c|$ for 2773 reflections will appear in the microfilm edition of this journal.

Discussion

Discrete cationic [Cu₂(tren)₂(CN)₂]²⁺ and anionic BPh₄⁻ units are found in the compound [Cu₂(tren)₂(CN)₂](BPh₄)₂. In Tables I and II are given the final positional parameters and temperature factors for [Cu₂(tren)₂(CN)₂]²⁺, while Table III lists the bonding distances and angles. The most outstanding feature of this dimeric cation is readily evident in Figure 1. The two trigonal-bipyramidal copper (tren)Cu-CN²⁺ moieties are interacting by means of two NH...NC hydrogen bonds. The NH...NC hydrogen-bond distance of 3.05 Å is a very reasonable distance for such a hydrogen bond.³⁵ Although the bridging hydrogen atom cannot be seen, its position can be calculated from the Cu-N-C(tren) angle to be ~ 0.05 Å from the N-N vector.

Hydrogen bonding between the ligands associated with two different transition metal complexes in the solid state

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Table III. Molecular Distances (Å) and Angles (deg) for $[\text{Cu}_2(\text{tren})_2(\text{CN})_2]^{2+}$ ^a

Distances			
Cu-Cu'	6.090 (1)	C1-C2	1.494 (10)
Cu-N1	2.076 (5)	C3-C4	1.493 (10)
Cu-N2	2.090 (5)	C5-C6	1.484 (10)
Cu-N3	2.119 (5)	C2-N2	1.451 (8)
Cu-N4	2.083 (5)	C4-N3	1.463 (10)
Cu-C7	1.967 (7)	C6-N4	1.451 (9)
N1-C1	1.494 (8)	C7-N5	1.127 (9)
N1-C3	1.485 (9)	N5-N4'	3.047 (7)
N1-C5	1.470 (8)		
Angles			
N1-Cu-N2	82.8 (2)	Cu-C7-N5	177.4 (6)
N1-Cu-N3	82.8 (2)	C1-C2-N2	109.1 (5)
N1-Cu-N4	83.2 (2)	C3-C4-N3	106.9 (6)
C7-Cu-N2	97.5 (2)	C5-C6-N4	107.8 (6)
C7-Cu-N3	99.0 (2)	C2-N2-Cu	107.9 (4)
C7-Cu-N4	94.9 (2)	C4-N3-Cu	105.3 (4)
N2-Cu-N3	112.5 (2)	C6-N4-Cu	107.2 (4)
N3-Cu-N4	120.4 (2)	C1-N1-C3	111.0 (5)
N2-Cu-N4	122.6 (2)	C1-N1-C5	110.7 (5)
C7-Cu-N1	177.9 (2)	C3-N1-C5	111.2 (5)
Cu-N1-C1	108.3 (4)	C7-N5-N4'	122.6 (5)
Cu-N1-C3	107.9 (4)	N5-N4'-C6'	114.3 (2)
Cu-N1-C5	107.5 (4)	N5-N4'-C6'	95.3 (4)

^a Estimated standard deviations of the least significant figures are in parentheses.

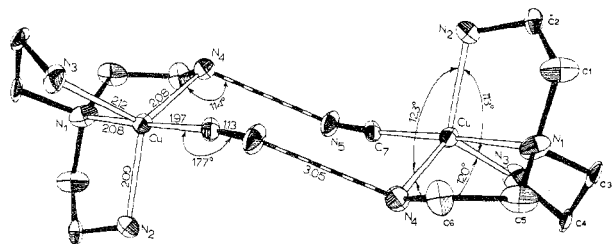


Figure 1. ORTEP plotting of $[\text{Cu}_2(\text{tren})_2(\text{CN})_2]^{2+}$ showing some of the geometrical parameters; the dimeric cation sits on a center of inversion. The tren intraligand bonds are shaded. Hydrogen atoms are not shown.

has been only infrequently noted in structure reports. For example, Gudel, *et al.*,³⁶ in their neutron diffraction study of $\text{D}_3\text{Co}(\text{CN})_6$ found that the slightly trigonally distorted $\text{D}_3\text{Co}(\text{CN})_6$ octahedra are three dimensionally linked by N-D-N bonds. In fact, their N-D-N distance (2.60 Å) is one of the shortest reported. Very recently the X-ray crystal structure of a five-coordinated copper(II) molecule was reported³⁷ where polymeric chains are formed by chloride in hydrogen bonding to the secondary nitrogen atoms on pairs of monomers. A dinuclear complex containing 2-aminoethanol, its anion, nickel(II), and cobalt(III) has been shown³⁸ to have dimeric $\text{Co}^{\text{III}}\cdots\text{Ni}^{\text{II}}$ cations consisting of octahedral tris chelates of cobalt(III) and nickel(II) held together by three hydrogen bonds between the oxygen faces of the octahedra. An interesting hydrogen-bonded square-planar copper dimer has been found by magnetic susceptibility studies to have an appreciable metal-metal interaction.³⁹

The importance of the hydrogen-bonding interaction in our $[\text{Cu}_2(\text{tren})_2(\text{CN})_2]^{2+}$ system is to be seen in the fact that, as indicated in the Introduction, we recently reported³⁰

(36) H. U. Gudel, A. Ludi, P. Fischer, and W. Haig, *J. Chem. Phys.*, **53**, 1917 (1970).

(37) N. A. Bailey, E. D. McKenzie, and J. M. Worthington, *J. Chem. Soc., Dalton Trans.*, 1227 (1973).

(38) J. A. Bertrand, W. J. Howard, and A. R. Kalyamaraman, *Chem. Commun.*, 437 (1971).

(39) J. A. Bertrand and F. T. Helm, *J. Amer. Chem. Soc.*, **95**, 8184 (1973).

Table IV. Temperature Factors^a for the Tetraphenylborate Anion ($\times 10^4$)

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
B	38 (4)	73 (8)	20 (2)	12 (5)	2 (2)	7 (3)
C11	39 (4)	81 (8)	14 (2)	-13 (5)	3 (2)	5 (3)
C12	62 (5)	90 (9)	24 (2)	2 (6)	7 (2)	-3 (4)
C13	43 (4)	65 (8)	26 (2)	3 (4)	3 (2)	2 (3)
C14	51 (4)	91 (9)	29 (2)	-20 (6)	16 (2)	1 (4)
C15	66 (5)	74 (9)	23 (2)	24 (5)	4 (2)	7 (3)
C16	83 (6)	60 (7)	24 (2)	-20 (6)	11 (3)	6 (3)
C21	38 (4)	61 (6)	22 (2)	-1 (4)	-6 (2)	1 (3)
C22	48 (4)	152 (9)	21 (2)	-7 (5)	2 (2)	6 (4)
C23	62 (5)	184 (11)	29 (2)	-12 (6)	-17 (3)	9 (4)
C24	88 (6)	114 (8)	18 (2)	-15 (6)	-10 (3)	3 (3)
C25	88 (6)	84 (8)	20 (2)	2 (5)	14 (3)	-1 (3)
C26	58 (4)	70 (7)	22 (2)	12 (4)	8 (2)	4 (3)
C31	37 (4)	65 (7)	17 (2)	-10 (4)	-1 (2)	3 (3)
C32	86 (5)	56 (7)	26 (2)	8 (5)	14 (3)	6 (3)
C33	90 (6)	92 (9)	29 (2)	5 (6)	28 (3)	5 (4)
C34	60 (5)	144 (11)	24 (2)	1 (6)	11 (3)	-15 (4)
C35	72 (5)	104 (9)	25 (2)	41 (5)	0 (3)	1 (4)
C36	75 (5)	81 (8)	18 (2)	23 (5)	7 (2)	11 (3)
C41	42 (4)	66 (7)	19 (2)	3 (4)	6 (2)	0 (3)
C42	50 (4)	79 (7)	26 (2)	5 (5)	-2 (3)	-3 (3)
C43	69 (6)	139 (10)	25 (2)	15 (6)	-8 (3)	-14 (4)
C44	44 (4)	154 (12)	44 (3)	-19 (6)	-6 (3)	-37 (5)
C45	67 (5)	104 (8)	38 (3)	-12 (6)	9 (3)	-8 (4)
C46	46 (4)	90 (8)	24 (2)	-11 (5)	2 (2)	0 (3)

^a The form of the anisotropic thermal ellipsoid is given by $B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl$.

the presence of an antiferromagnetic exchange interaction for this outer-sphere dimer. A characterization of the electronic exchange properties of such a dimer is tantamount to an investigation of the rate of an outer-sphere electron-transfer process between Cu(II) centers as it occurs in the *solid* state. There has been, of course, a considerable amount of work on outer-sphere electron-transfer reactions in *solution*.⁴⁰ It may be that a hydrogen-bonding interaction very similar to one in $[\text{Cu}_2(\text{tren})_2(\text{CN})_2]^{2+}$ will prove to be the pathway for many solution outer-sphere redox reactions. Various workers⁴¹⁻⁴³ have in fact suggested that the role of water in the outer-sphere electron-transfer reactions of transition metal ions is to establish a hydrogen-bonded pathway between the hydration shells of the two ions. This pathway could support the electron transfer which may or may not be followed by transfer of a hydrogen ion. The role of cyanide ion as an electron mediator in solution inner-sphere redox reactions has been supported.¹⁶⁻¹⁸ As with the outer-sphere cyanide case it is to a large degree the extent of electron exchange propagated by the bridge that determines the rate of electron transfer.

The overall stereochemistry of the copper atoms and their orientation with respect to the hydrogen bridges is of general concern. Bond distances and angles for $[\text{Cu}_2(\text{tren})_2(\text{CN})_2]^{2+}$ are given in Table III. The copper atoms (see Figure 1) are trigonal bipyramidally coordinated with the tren ligand providing four nitrogen atoms with Cu-N distances ranging from 2.08 to 2.12 Å. The cyanide ion is bonded in an axial position in an essentially linear fashion (Cu-C-N = 177.4 (6)°), the small deviation from linearity perhaps re-

(40) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions. A Study of Metal Complexes in Solution," 2nd ed, Wiley, New York, N. Y., 1968, pp 454-525.

(41) D. R. Stranks in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience, New York, N. Y., 1960, p 78.

(42) W. L. Reynolds and R. Lumry, *J. Chem. Phys.*, **23**, 2560 (1955).

(43) R. A. Horne and E. B. Axelrod, *J. Chem. Phys.*, **40**, 1519 (1964).

Table V. Positional Parameters for Tetraphenylborate Atoms

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
B	0.7373 (5)	0.2803 (6)	0.1188 (3)
C11	0.7300 (4)	0.1228 (5)	0.1213 (2)
C12	0.6386 (4)	0.0623 (7)	0.1155 (3)
C13	0.6280 (4)	-0.0693 (7)	0.1120 (3)
C14	0.7057 (6)	-0.1487 (6)	0.1142 (3)
C15	0.7972 (5)	-0.0949 (6)	0.1190 (3)
C16	0.8077 (4)	0.0380 (5)	0.1229 (3)
C21	0.7105 (4)	0.3149 (5)	0.0396 (3)
C22	0.6170 (4)	0.3382 (6)	0.0138 (3)
C23	0.5927 (5)	0.3552 (7)	-0.0528 (4)
C24	0.6617 (6)	0.3461 (6)	-0.0964 (3)
C25	0.7553 (5)	0.3207 (6)	-0.0738 (3)
C26	0.7807 (4)	0.3069 (5)	-0.0063 (3)
C31	0.6597 (4)	0.3500 (5)	0.1647 (3)
C32	0.6269 (5)	0.2959 (5)	0.2211 (3)
C33	0.5638 (5)	0.3594 (7)	0.2608 (3)
C34	0.5347 (4)	0.4779 (8)	0.2468 (3)
C35	0.5672 (5)	0.5393 (6)	0.1932 (3)
C36	0.6279 (5)	0.4772 (6)	0.1536 (3)
C41	0.8411 (4)	0.3401 (5)	0.1470 (3)
C42	0.8925 (4)	0.2905 (6)	0.2038 (3)
C43	0.9731 (5)	0.3475 (8)	0.2342 (3)
C44	1.0094 (5)	0.4598 (8)	0.2083 (4)
C45	0.9641 (5)	0.5124 (6)	0.1525 (4)
C46	0.8812 (4)	0.4528 (6)	0.1235 (3)

Table VI. Distances (Å) and Angles (deg) for the Tetraphenylborate Anion

Distances		
B-C11	1.633 (8)	C31-C32 1.382 (8)
B-C21	1.663 (9)	C32-C33 1.394 (10)
B-C31	1.638 (8)	C33-C34 1.314 (11)
B-C41	1.624 (8)	C34-C35 1.365 (10)
		C35-C36 1.364 (9)
C11-C12	1.405 (8)	C36-C31 1.399 (8)
C12-C13	1.369 (10)	
C13-C14	1.348 (10)	C41-C42 1.404 (8)
C14-C15	1.377 (10)	C42-C43 1.365 (9)
C15-C16	1.383 (8)	C43-C44 1.384 (11)
C16-C11	1.382 (8)	C44-C45 1.366 (11)
		C45-C46 1.390 (9)
C21-C22	1.376 (8)	C46-C41 1.391 (8)
C22-C23	1.381 (10)	
C23-C24	1.351 (10)	
C24-C25	1.383 (10)	
C25-C26	1.399 (9)	
C26-C21	1.396 (8)	
Angles		
C11-B-C21	103.5 (4)	C32-C31-C36 113.3 (5)
C11-B-C31	112.2 (5)	C31-C32-C33 123.5 (7)
C11-B-C41	115.0 (5)	C31-C36-C35 123.1 (6)
C21-B-C31	110.4 (4)	C32-C33-C34 120.5 (7)
C21-B-C41	112.8 (5)	C33-C34-C35 119.5 (7)
C31-B-C41	103.1 (4)	C34-C35-C36 120.3 (6)
C12-C11-C16	114.2 (5)	C42-C41-C46 113.5 (5)
C11-C12-C13	122.6 (6)	C41-C42-C43 124.0 (6)
C11-C16-C15	123.4 (5)	C41-C46-C45 124.1 (6)
C12-C13-C14	121.5 (6)	C42-C43-C44 119.7 (7)
C13-C14-C15	118.6 (6)	C43-C44-C45 119.5 (5)
C14-C15-C16	119.8 (6)	C44-C45-C46 119.2 (6)
C22-C21-C26	115.6 (5)	
C21-C22-C23	123.2 (6)	
C21-C26-C25	120.9 (5)	
C22-C23-C24	120.1 (7)	
C23-C24-C25	119.3 (6)	
C24-C25-C26	120.7 (6)	

flecting the hydrogen bonding interaction at the other end of the cyanide. The CuNC, NCC, and CNC angles in the Cu(tren) system are all close to 109°, indicating an essentially unstrained tren ligand.

A comparison of M-N bond distances for this Cu(tren) moiety with those⁴⁴ for the Ni(tren) moiety in [Ni₂(tren)₂-

(44) D. M. Duggan and D. N. Hendrickson, *Inorg. Chem.*, in press.

Table VII. Least-Squares Planes for the Tetraphenylborate Phenyl Rings with Deviations and Estimated Errors in Angstroms, the Equation of the Plane Being $Ax + By + Cz - D = 0$

Plane 1: $A = 0.0673, B = 0.0446, C = -0.9967, D = -1.724$							
Atom	C11	C12	C13	C14	C15	C16	B
Distance	-0.002	0.002	0.002	-0.006	0.006	-0.001	0.128
Error	0.005	0.005	0.006	0.006	0.005	0.005	0.007
Plane 2: $A = 0.6180, B = -0.5439, C = -0.5676, D = 3.4320$							
Atom	C41	C42	C43	C44	C45	C46	B
Distance	-0.004	0.008	-0.004	-0.003	0.006	-0.003	-0.202
Error	0.005	0.006	0.007	0.008	0.007	0.006	0.006
Plane 3: $A = -0.1624, B = -0.9828, C = -0.0871, D = -4.849$							
Atom	C21	C22	C23	C24	C25	C26	B
Distance	-0.001	0.009	-0.007	-0.003	-0.011	-0.008	0.168
Error	0.005	0.007	0.007	0.007	0.006	0.005	0.006
Plane 4: $A = -0.7510, B = -0.3547, C = -0.5567, D = -9.806$							
Atom	C31	C32	C33	C34	C35	C36	B
Distance	0.018	-0.016	0.002	0.011	-0.008	-0.006	-0.064
Error	0.005	0.006	0.007	0.007	0.007	0.006	0.006
Dihedral Angles							
Ring A	Ring B	∠AB, deg	Ring A	Ring B	∠AB, deg		
1	2	54.3	2	3	61.1		
1	3	88.2	2	4	87.4		
1	4	60.8	3	4	58.7		

(NCO)₂]²⁺ is interesting. The nickel atoms are octahedrally coordinated by virtue of di-μ-NCO⁻ bridging. There does not seem to be any clear indication of a difference in degree of strain in the tren ligand in the two systems. This is also true of the [Cu₂(tren)₂(NCO)₂]²⁺ dimer in [Cu₂(tren)₂(NCO)₂](BPh₄)₂, the structure of which is currently being completed. Thus, even though the packing of [M₂(tren)₂(NCO)₂]²⁺ and BPh₄⁻ ions would have been expected to be very similar for either M = Cu(II) or M = Ni(II), the copper atoms prefer to be of trigonal-bipyramidal geometry. For the copper cyanide compound the average Cu-N(tren) distance is 2.092 ± 0.014 Å. In the case of the two cyanates, the average Cu-N(tren) distance is 2.083 ± 0.016 Å and the average Ni-N(tren) distance is 2.082 ± 0.031 Å. There is a curious observation to be made with respect to M-N(tren) distances in these three complexes. Both of the Cu-tren complexes have as the shortest Cu-N(tren) distance that to the tertiary tren nitrogen, whereas in [Ni₂(tren)₂(NCO)₂](BPh₄)₂ this Ni-N(tren) bond to the tertiary nitrogen is by far the longest of the Ni-N(tren) distances. This is probably a reflection of the difference between the stereochemical requirements of five- and six-coordination. There are two reported structures that can be used to check the generality of this observation. The Cu-N(tren) tertiary nitrogen bond in [Cu(tren)(NCS)](SCN)⁴⁵ is the shortest (2.04 vs. 2.06, 2.07, 2.16 Å), which is in agreement with the above observations. On the other hand, the Ni-N(tren) distance to the tertiary nitrogen in Ni(tren)(NCS)₂⁴⁶ is not the longest (2.11 vs. 2.11, 2.15, and 2.16 Å). This last structure, however, is probably of lower quality in that small (712 and 383 reflections) data sets from two previous determinations were combined in the calculation. While small specific differences are probably not statistically significant, the general trend in tertiary five-coordinate vs. six-coordinate tren systems is probably correct in general.

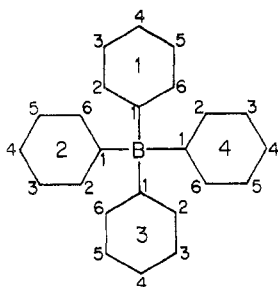
Another important aspect of the structure of [Cu₂(tren)₂(CN)₂]²⁺ is the disposition of the cyanide ion. In the Prussian blue analogs the C-N distances are not known very ac-

(45) P. C. Jain and E. C. Lingafelter, *J. Amer. Chem. Soc.*, 89, 724 (1967).

(46) P. D. Cradwick and D. Hall, *Acta Crystallogr., Sect. B*, 26, 1384 (1970).

curately.⁷ They range from ~ 1.12 to ~ 1.14 Å. In $\text{Cu}_3(\text{NH}_3)_3(\text{CN})_4$ ²⁸ two of the three crystallographically different cyanide groups are disordered, but for the ordered cyanide C-N = 1.151 (9) Å. Perhaps the best bridging cyanide bond determination is to be found in the structure report²² for $(\text{NH}_3)_5\text{CoN-CCo}(\text{CN})_5 \cdot \text{H}_2\text{O}$. In this system the cyanide is ordered and C-N = 1.152 (5) Å. The terminal C-N bond lengths in this same compound range from 1.135 (5) to 1.154 (5) Å. Thus, considering the accuracy associated with our C-N = 1.127 (9) Å bond distance for $[\text{Cu}_2(\text{tren})_2(\text{CN})_2](\text{BPh}_4)_2$ and the range of C-N bond lengths for the variety of systems listed above as well as for other transition metal compounds (see references in ref 22), it is concluded that little is to be learned from C-N lengths in general and that this distance in our system is "normal."

Positional parameters, temperature factors, and bonding angles and distances for the tetraphenylborate anion are given in Tables IV-VI. The numbering scheme used is illustrated in the diagram



The general structural features of the tetraphenylborate in this system are similar to those found previously in others.^{44,47} The ring angles at the site of boron binding are

(47) M. DiVaira and A. B. Orlandini, *J. Chem. Soc., Chem. Commun.*, 1704 (1972).

small ($\sim 114^\circ$), while those adjacent to this are large ($\sim 123^\circ$), and the boron atom lies out of the plane of each phenyl ring (see Table VII) by anywhere from 0.06 to 0.20 Å. The dihedral angles between the phenyl rings as usual show a wide range, apparently adjusting in order to pack most efficiently into the lattice.

In order to estimate the configuration stability of the tetraphenylborate anion, internuclear repulsion energies were calculated as described in previous publications.^{44,47} These calculations sum the potential energy $U_{ij} = a_{ij}[\exp(-b_{ij}r_{ij})] - c_{ij}r_{ij}^{-6}$ over all C-H, C-C, and H-H pairs in the anion. When the total potential energy of the anion in this system is compared to that found⁴⁴ for $[\text{Ni}_2(\text{tren})_2(\text{NCO})_2](\text{BPh}_4)_2$, the difference is 3 kcal/mol with the copper system being less stable. This conformational instability of the tetraphenylborate may be taken as a reflection of the relative structural integrity of the $[\text{Cu}_2(\text{tren})_2(\text{CN})_2]^{2+}$ cation and the overall stability of the lattice packing.

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Registry No. $[\text{Cu}_2(\text{tren})_2(\text{CN})_2](\text{BPh}_4)_2$, 51464-43-8.

Supplementary Material Available. The final values of $|F_o|$ and $|F_c|$ for 2773 reflections will appear following these pages in the microfilm edition of this 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-74-1911.

Contribution from the Transuranium Research Laboratory, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

Crystal Structure of Neodymium Tris(methylcyclopentadienide)¹

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The crystal structure of neodymium tris(methylcyclopentadienide) was determined by single-crystal X-ray diffraction methods. Crystals are monoclinic, space group $P2_1/c$, and the unit cell dimensions are $a = 14.257$ (5) Å, $b = 26.85$ (1) Å, $c = 9.286$ (3) Å, $\beta = 120^\circ 17$ (5)'; $Z = 8$. The structure was determined by Patterson and Fourier methods and was refined by the method of least squares to an agreement index of 0.040 using 3463 observations and 349 variables. Each Nd atom is η^5 -bonded to three cyclopentadienide rings and η^1 -bonded to another ring of an adjacent $(\text{C}_6\text{H}_7)_3\text{Nd}$ group. This sharing of a C atom between two Nd atoms is repeated in a manner which produces tetrameric units: $[(\text{C}_6\text{H}_7)_3\text{Nd}]_4$. The types of Nd-C bonds found in this structure are in accord with the idea that lanthanide-cyclopentadienide organometallic bonds are mainly ionic in nature.

Introduction

There has been interest in the nature of the bonding between 4f and 5f metals and aromatic organic ligands since Birmingham and Wilkinson³ first prepared the cyclopenta-

dienides of Sc and the lanthanide elements and Reynolds and Wilkinson⁴ synthesized tris(cyclopentadienyl)uranium chloride. The chemical behavior of the former clearly indicated ionic bonding in it while the latter appeared somewhat covalent. These authors suggested that structural data would be useful in confirming this and for the latter assumed a structure in

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(3) J. M. Birmingham and G. Wilkinson, *J. Amer. Chem. Soc.*, **78**, 42 (1956).

(4) L. T. Reynolds and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2**, 246 (1956).