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Magnetic Exchange Interactions in Transition Metal Dimers. VII. X-Ray Structural Characterization of Three Outer-Sphere Copper(II) Dimers $[Cu_2(tren)_2X_2](BPh_4)_2$ Where $X^- = Cl^-$, NCO^-, and NCS^-. Outer-Sphere Electron Exchange Interactions

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The structures of three tetraphenylborate salts of outer-sphere-associated copper(II) dimers, $[Cu_2(tren)_2Cl_2](BPh_4)_2$, $[Cu_2(tren)_2(NCO)_2](BPh_4)_2$, and $[Cu_2(tren)_2(NCS)_2](BPh_4)_2$, have been determined using heavy-atom least-squares X-ray methods in conjunction with data measured on four-circle diffractometers to the following conventional observed–calculated agreement factors: chloride, $R_F = 0.048$ and $R_{wF} = 0.071$ for 3527 observed (2σ) reflections; cyanate, $R_F = 0.075$ and $R_{wF} = 0.054$ for 1212 observed (2σ) reflections; thiocyanate, $R_F = 0.071$ and $R_{wF} = 0.080$ for 3142 observed (2σ) reflections. All three compounds crystallize in the $P2_1/c$ space group with two formula weights in a cell and the unit cell parameters are as follows: chloride, $a = 13.678$ (5) Å, $b = 10.288$ (3) Å, $c = 20.432$ (6) Å, $\beta = 94.84$ (3)°; cyanate, $a = 14.003$ (6) Å, $b = 10.399$ (5) Å, $c = 20.436$ (9) Å, $\beta = 94.00$ (3)°; thiocyanate, $a = 14.977$ (5) Å, $b = 9.764$ (2) Å, $c = 21.226$ (6) Å, $\beta = 98.79$ (3)°. The crystal densities are as follows: chloride, 1.28 (calcd) and 1.30 (2) g/cm^3 (obsd); cyanate, 1.28 (calcd) and 1.27 (2) g/cm^3 (obsd); thiocyanate, 1.24 (calcd) and 1.25 (2) g/cm^3 (obsd). The compounds $[Cu_2(tren)_2Cl_2](BPh_4)_2$, $[Cu_2(tren)_2(NCO)_2](BPh_4)_2$, and $[Cu_2(tren)_2(NCS)_2](BPh)_2$, where tren is 2,2',2''-triaminotriethylamine, are tetraphenylborate salts of outer-sphere dimers of chloro-2,2'2''-triaminotriethylaminecopper(II), (cyanato-*N*)-2,2'-2''-triaminotriethylaminecopper(II), and (thiocyanato-*N*)-2,2',2''-triethylaminecopper(II), respectively. In each case discrete $[Cu_2(tren)_2X_2]^{2+}$ and BPh_4^- units are found wherein each copper atom in the cation is trigonal-bipyramidally coordinated with tren occupying four sites and with an axially bonded X group (nitrogen end of NCO^- and NCS^-). The copper trigonal bipyramids are distorted in each case from perfect threefold symmetry with trigonal-plane angles of ~111–112, ~120, and ~124°. The $[Cu_2(tren)_2X_2]^{2+}$ ions are dimeric by virtue of the fact that the coordinated X^- group on each copper atom is hydrogen bonding to a primary amine of the tren ligand coordinated to the second copper atom, i.e., Cu–X···HN–Cu. The cyanate (thiocyanate) groups are hydrogen bonding in an end-to-end fashion employing the oxygen (sulfur) atom. The dimeric cations are located on centers of inversion in the unit cells and the Cu–Cu distances are as follows: chloride, 5.7994 (6) Å; cyanate, 6.537 (3) Å; thiocyanate, 6.136 (1) Å. Variable-temperature (4.2–296°K) magnetic susceptibility data are presented for $[Cu_2(tren)_2Cl_2](BPh_4)_2$ and the isostructural $[Cu_2(tren)_2Br_2](BPh_4)_2$ and $[Cu_2(tren)_2(OH)_2](BPh_4)_2$ compounds. All three compounds show an antiferromagnetic exchange interaction and least-squares fitting to the Bleaney–Bowers isotropic exchange equation gives the following parameters: Br^-, $J = 3.5$ cm^{-1}; Cl^-, $J = 3.2$ cm^{-1}; OH^-, $J = 2.1$ cm^{-1}. The range of exchange interactions in the series $[Cu_2(tren)_2X_2](BPh_4)_2$, where $X^- = Br^-$, Cl^-, OH^-, CN^-, NCO^- (two crystalline forms), and NCS^-, is discussed and shown to give some insight into a potential cause of anion assistance effects in solution outer-sphere redox processes.

Introduction

Copper complexes have infrequently been reported to have trigonal-bipyramidal (TBP) geometry. The compound $Cu(NH_3)_2Ag(SCN)_3$ has been reported[4] to have a structure wherein $Cu(NH_3)_2(NCS)_3^-$ moieties have regular TBP copper coordination geometry, whereas the cation in $[Cu(bpy)_2I]I$ has been found[5] to have a distorted TBP copper geometry. Distorted TBP copper symmetry has very recently been reported[6] for the copper ions in the dimeric cation of $[Cu_2([14]4,11\text{-diene-}N_4)_2CN](ClO_4)_3$, where [14]4,11-diene-N$_4$ is the macrocyclic ligand 5,7,7,12,14,14-hexamethyl-1,4,8,-11-tetraazacyclotetradeca-4,11-diene. It could be anticipated that, with various tripodal tetradentate ligands, TBP copper complexes would be found. For example, the structure[7] of $[Cu(Me_6tren)Br]Br$, where Me$_6$tren is the nitrogen-methylated derivative of tren (2,2',2''-triaminotriethylamine), does show TBP copper ions.

We have very recently reported[8] the X-ray structure of $[Cu_2(tren)_2(CN)_2](BPh_4)_2$, the tetraphenylborate salt of an outer-sphere-bridged copper dimer which possesses an antiferromagnetic exchange interaction ($J = -1.8$ cm^{-1}) propagated by two hydrogen bonds of the type Cu–CN···HN–Cu.[6] In this paper we are reporting the single-crystal X-ray structures of the analogous compounds $[Cu_2(tren)_2Cl_2](BPh_4)_2$, $[Cu_2(tren)_2(NCO)_2](BPh_4)_2$, and $[Cu_2(tren)_2(NCS)_2](BPh_4)_2$. Singlet-to-triplet EPR transitions have been noted[9,10] for the outer-sphere dimers in the cyanate and thiocyanate compounds, and from the positions of these EPR transitions J values in the range of 0.05–0.16 cm^{-1} were deduced. In this paper, we are reporting variable-temperature magnetic susceptibility data for the chloride compound and for the analogous bromide and hydroxide compounds. The change in exchange interaction throughout the series of outer-sphere copper dimers will be shown to point to one possible explanation for *anion assistance* effects seen in outer-sphere *solution* redox processes.

Experimental Section

Compound Preparation. Powder samples of $[Cu_2(tren)_2X_2](BPh_4)_2$ where $X^- = NCO^-$ and NCS^- were prepared as reported[9] and crystals were grown by slow evaporation of an acetonitrile solution. Form I of the cyanate is studied in this paper. Crystals of $[Cu_2(tren)_2Cl_2](BPh_4)_2$ were also obtained by slow evaporation of an acetonitrile solution; however, the powder sample was obtained in a procedure modified (more concentrated solutions with some ethanol present) from that used for the other two compounds. In the preparation of the chloride compound 2.50 g of $CuSO_4 \cdot 5H_2O$ was dissolved in ~25 ml of H_2O to which was then added ~1.5 ml of tren. A solution of 0.60 g of NaCl dissolved in ~25 ml of H_2O was added and the resulting solution was filtered. Addition of a ~25-ml 50% ethanol–water solution of 0.25 g of $NaBPh_4$ to the filtrate gave an immediate precipitation of the desired compound which was washed with considerable H_2O and then with ether and finally was dried in vacuo over P_2O_5 overnight. A powder sample of $[Cu_2(tren)_2Br_2](BPh_4)_2$ was prepared by a similar procedure, while the powder of $[Cu_2(tren)_2(OH)_2](BPh_4)_2$ was prepared by a slight modification of the previous procedure[9] wherein the initial pH of the solution was adjusted to 9.5 with NaOH and then the solution was filtered into a stirred aqueous solution of $NaBPh_4$. All compounds gave excellent analytical data (see Table I[11]).

A nitrogen-deuterated sample of $[Cu_2(tren\text{-}d_6)_2(NCO)_2](BPh_4)_2$ was prepared in the same manner as for the undeuterated material except D_2O was used as a solvent in place of H_2O. The nitrogenous hydrogen atoms of tren exchange rapidly with the deuterium atoms in the basic aqueous media. The success of the deuteration was gauged by a Nujol mull ir spectrum which showed no N–H modes and by H–D chemical analyses performed by Mr. J. Nemeth in our microanalytical laboratory.

Susceptibility and EPR. Variable-temperature magnetic susceptibility and EPR measurements were made as indicated in a previous paper.[9] Least-squares fitting to the Bleaney–Bowers[12] equation for isotropic exchange interaction in a copper dimer was effected with the computer program STEPT.[13]

Crystal Measurements. All structure solutions and refinements were carried out at the University of Illinois. The diffraction data for $[Cu_2(tren)_2Cl_2](BPh_4)_2$ and $[Cu_2(tren)_2(NCS)_2](BPh_4)_2$ were collected by Molecular Structure Corp., while the smaller data set for $[Cu_2(tren)_2(NCO)_2](BPh_4)_2$ was collected at the University of Illinois.

A blue-green prismatic crystal of **$[Cu_2(tren)_2Cl_2](BPh_4)_2$** measuring 0.40 × 0.45 × 0.70 mm was mounted on a thin glass fiber with a random crystal orientation. Preliminary examination of the crystal and data collection were performed on a Syntex $P\bar{1}$ computer-controlled diffractometer equipped with a graphite-crystal incident-beam monochromator. For the location of a set of starting reflections the diffractometer setting angles were positioned at $2\theta = \omega = \chi = 0°$ and a Polaroid film cassette was mounted in front of the counter. The film was exposed to Mo Kα radiation for 15 min while the ϕ axis was rotated through 360° at 192°/min. The x and y coordinates of 15 reflections were measured from this film and these were used with the Syntex software package to center the reflections automatically. The setting angles for the reflections were used as input for the autoindexing program which is used to select the best unit cell. The crystal was found to be monoclinic and the space group was determined as $P2_1/c$ [systematic absences are $0k0$, $k = 2n + 1$, and $h0l$, $l = 2n + 1$] with cell constants determined from a least-squares refinement of the setting angles for the 15 strong reflections as $a = 13.678$ (5) Å, $b = 10.288$ (3) Å, $c = 20.432$ (6) Å, $\beta = 94.84$ (3)°, and $V = 2865$ (2) Å^3. Using these parameters and mol wt 1100.9 leads to the density ρ(calcd) = 1.28 g/cm^3 ($Z = 2$ dimers) compared with ρ(obsd) = 1.30 (2) g/cm^3 (toluene–bromotoluene flotation). The width at half-height for ω scans of several strong reflections was 0.17°.

Intensity data were collected for $[Cu_2(tren)_2Cl_2](BPh_4)_2$ at 22 ± 1° with Mo Kα radiation using the θ–2θ scan technique and a variable scan rate of 3.0–24.0°/min depending on the intensity of the reflection. A symmetrical scan range of 2θ(Mo Kα_1) − 0.7° to 2θ(Mo Kα_2) + 0.7° was used to measure 3749 unique reflections up to a maximum 2θ of 45°. Stationary-crystal, stationary-counter background counts were taken at each end of the scan range; the ratio R of scan time to background counting time was 2.0. The Syntex data collection program corrects the scan count for background, and for intense reflections a coincidence correction is automatically applied to the data. The counter was placed 19 cm from the crystal with the counter aperature wide open at its 2-mm diameter. An X-ray beam collimator with a 1.5-mm opening was used. The takeoff angle going into the monochromator was set at 3° and the width of the pulse height analyzer was set to accept about 95% of the radiation when centered on the Mo Kα peak. Three standard reflections were measured after every 100 reflections to check that crystal and electronic stability and deviations from the average intensity did not differ significantly from that expected on the basis of counting statistics alone. Extinction corrections were not applied and no absorption corrections were made in view of the small variation in transmission factors (67.9 ± 1.6%) through the extreme directions of the crystal during data collection. In the refinement of the structure 3527 reflections having $F_o > 2\sigma(F_o)$ were used. Here $\sigma(F_o)$ is the standard deviation for the observed intensity of a reflection and is calculated from the formula $\sigma(F_o) = (^1/_2F_o)[S^2(C + R^2B) + (pF_o{}^2)^2]^{1/2}$ where S is the scan rate, C is the total integrated peak count, R is defined above, and B is the total background count. The parameter p used in the calculation of standard deviation in this case was set equal to 0.07.

A green prismatic crystal of **$[Cu_2(tren)_2(NCS)_2](BPh_4)_2$** measuring 0.22 × 0.26 × 0.36 mm was mounted on a thin glass fiber with the long direction parallel to the glass fiber. Crystal alignment and cell parameter determination were effected as described above for the chloride. The thiocyanate compound is also monoclinic with space group $P2_1/c$ and $a = 14.977$ (5) Å, $b = 9.764$ (2) Å, $c = 21.226$ (6) Å, $\beta = 98.79$ (3)°, and $V = 3067$ (2) Å^3. Using these parameters and mol wt 1146.2 leads to the density ρ(calcd) = 1.24 g/cm^3 ($Z = 2$ dimers) compared with ρ(obsd) = 1.25 (2) g/cm^3. In this case the width at half-height for ω scans of several strong reflections was 0.14°. Intensity data were collected for the thiocyanate compound at 21 ± 1° in a fashion identical with that used for the chloride, except the ratio R of scan time to background counting time was 4.0. There were 4040 unique reflections in the range $0° < 2\theta \leq 45°$. An extinction correction was not applied and absorption corrections were deemed unnecessary in light of the small variation in transmission factors (81.9 ± 1.4%) through the extreme directions of the crystal during data collection. For the thiocyanate, $p = 0.06$. In the refinement of the thiocyanate structure 3142 reflections having $F_o > 2\sigma(F_o)$ were used.

A needlelike blue crystal of **$[Cu_2(tren)_2(NCO)_2](BPh_4)_2$** was found to have $P2_1/c$ space group symmetry with the b^* axis of the reciprocal cell lying along the needle axis. It must be recalled that there are two crystalline forms of copper cyanate and this one we have called form I.[9] The crystal was 0.4 × 0.2 × 0.2 mm and mounted on the needle axis for data collection, which was carried out using a computer-controlled Picker FACS-1 diffractometer. Because the reflections were weak for this crystal, data were only collected between $2\theta = 10°$ and $2\theta = 35°$. The θ–2θ scan technique was used with a base width of 2.1° and a scan rate (not variable) of 1°/min. Dispersion corrections were made to account for Mo Kα_1–Kα_2 splitting at high angles. A zirconium foil filter was used to remove the $K\beta$ radiation. Centering 15 strong reflections by hand allowed refinement of the unit cell parameters to their final values of $a = 14.003$ (6) Å, $b = 10.399$ (5) Å, $c = 20.436$ (9) Å, and $\beta = 94.00$ (3)°. Using these parameters and a mol wt 1141.9 leads to the density ρ(calcd) = 1.28 g/cm^3 ($Z = 2$ dimers) compared with ρ(obsd) = 1.27 (2) g/cm^3. A total of 1912 unique reflections were collected at room temperature, of which 1212 were observed at the $I > 2\sigma(I)$ level, where in this case $\sigma(I) = [C + R^2B]^{1/2}$. Lorentz and polarization corrections were applied to the data at the start of the calculations; however, again absorption corrections were not applied because of a small variation in transmission factors (82.7 ± 2.7%) in data collection. Standard deviations were assigned to the structure factors on the basis of counting statistics: $\sigma(|F|) = (|F|/2I)[C + 0.25R^2B + (0.02I)^2]^{1/2}$.

Structure Solutions and Refinements. The structure of $[Cu_2(tren)_2Cl_2](BPh_4)_2$ was solved by the trivial approach of using the atomic coordinates, excluding those of the cyanide bridge, from the structure determination of $[Cu_2(tren)_2(CN)_2](BPh_4)_2$. Generation of a Fourier map from these atomic positions (the spherical atom scattering factors used in this and following calculations are those reported by Hansen et al.,[14] for Cu, N, B, Cl, O, and H and by Cromer and Mann[15a] for S and C, while values for anomolous dispersion factors for Cu, Cl, and S were taken from ref 15b) and the 3527 reflections at the 2σ cutoff led to the location of the chlorine atom. With all the nonhydrogen atom positions included, six cycles of least-squares refinement with isotropic thermal parameters using the computer program ORFLS (written by Busing and Levy) were calculated. The function minimized was $\sum w = (|F_o| - |F_c|)^2$, where $w = 1/(\sigma(F_o))^2$. The unweighted and weighted agreement factors at this point were $R_F = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.096$ and $R_{wF} = (\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2)^{1/2} = 0.143$ and the refinement had converged. Because of program limits (270 parameters), it was necessary to carry out anisotropic refinements varying either the cation or the anion parameters separately. Thus, one cycle of anisotropic refinement was carried out varying the cation parameters, followed by two cycles of anisotropic refinement of the anion parameters. Hydrogen atoms were added to the model at this time. Because the positions of all of the hydrogen atoms were not clearly indicated on a difference Fourier, they were generated using the program HYGEN.[16] In this procedure, it is assumed that all carbon and nitrogen atoms in the tren ligand are sp^3 hybridized, while the benzene moieties possess trigonal hybridization. Carbon–hydrogen and nitrogen–hydrogen distances were all taken as 0.95 Å. The temperature factors used for the hydrogen atoms (not varied) are those of the atoms to which they are attached as calculated from the isotropically refined model. After two more anisotropic cycles varying the parameters of the dimeric cation and two more anisotropic cycles varying the parameters of the anion, the refinement had converged to a final fit of $R_F = 0.048$ and $R_{wF} = 0.071$, and the ERF (expected error in a measurement of unit weight) was 1.85. A final difference Fourier shows no peaks or holes greater than 0.55 e/Å^3 in any region. The final values of $|F_o|$ and $|F_c|$ for the 3527-reflection 2σ cutoff data set will appear as supplementary material.

In the structure solution of **$[Cu_2(tren)_2(NCO)_2](BPh_4)_2$**, a Patterson function was calculated using the 1212 observed reflections, and heavy-atom vectors were found at the $(0, {}^1/_2 - y, {}^1/_2)$, $(2\bar{x}, {}^1/_2, {}^1/_2 - 2z)$, and $(2x, 2y, 2z)$ positions corresponding to $x = 0.171$, $y = 0.092$, and $z = 0.108$. This placed one copper atom 6.58 Å from another which is related to it by a center of inversion. The copper atom position was used to generate a Fourier map which revealed 12 peaks above 5.0 e/Å^3 other than the metal position and these were set as carbon atoms to generate a second Fourier which showed all of the nonhydrogen BPh_4 atoms. The positional and isotropic thermal parameters of the BPh_4^- and metal atoms were refined by one least-squares fit to the data, and using this 26-atom model, a third Fourier was generated where all nonhydrogen dimer atoms were located. A sequence of three least-squares calculations with isotropic temperature factors on all atoms gave an agreement with the observed data of $R_F = 0.109$ and $R_{wF} = 0.089$ with ERF = 2.03. After two cycles of refinement with the dimeric cation having anisotropic thermal parameters (we elected, at first, to keep the BPh_4^- parameters isotropic because of the small number of reflections), all hydrogen atom positions were calculated. With the hydrogen atoms included, refinement of the cation with anisotropic thermal parameters coupled with refinement of the anion with isotropic thermal parameters gave convergence at $R_F = 0.083$ and $R_{wF} = 0.071$. It was found that one atom, C(7), the central carbon atom of the cyanate group, had a non-positive-definite thermal tensor. In order to trace the source of the trouble with C(7) and possibly to alleviate the problem, the cyanate atoms were removed from the structure and a difference Fourier was calculated. From this map, no sign of positional disorder in any of the three atoms of the cyanate could be found. The cyanate atoms were put back in and the structure was refined varying anisotropic parameters for the nonhydrogen BPh_4^- atoms *and* anisotropic parameters for the C(7) atom. This yielded non-positive-definite thermal tensors for both the C(7) and boron atoms. The thermal parameters for both the C(7) and boron atoms were then taken as isotropic and the parameters of the BPh_4^- anion were varied in two more least-squares cycles. Both the C(7) and the boron atom had positive-definite thermal tensors. With the C(7) atom still isotropic, the cation parameters were twice cycled to converge with $R_F = 0.075$, $R_{wF} = 0.054$, and ERF = 1.21. The final values of $|F_o|$ and $|F_c|$ for the 1212-reflection 2σ cutoff data set will appear as supplementary material.

Initially a solution of the structure of $[Cu_2(tren)_2(NCS)_2](BPh_4)_2$ was attempted by using the atomic coordinates of the cyanate, but this failed. Investigation of the Patterson function generated with the 3142 reflections at the 2σ cutoff level showed that the copper atom is located at $x = 0.153$, $y = 0.093$, and $z = 0.105$ which gives a Cu–Cu distance of 6.41 Å. A Cu–Cu distance shorter than that found for the cyanate was not expected. A difference Fourier map based on the Cu position showed all but four nonhydrogen atoms and these were located in the second difference Fourier map. With all of the nonhydrogen atom positions included, five cycles of least-squares refinement with isotropic thermal parameters were calculated resulting in $R_F = 0.118$ and $R_{wF} = 0.138$. This was followed by one cycle of refinement with anisotropic thermal parameters for the anion, followed by one with anisotropic thermal parameters for the dimeric cation. Hydrogen atom positions were then calculated and added to the model with isotropic thermal parameters taken as equal to those of the atoms to which they are bonded as calculated from the isotropically refined model. After one anisotropic cycle each on the anion and dimeric cation, successively, the structure converged to a final fit of $R_F = 0.071$, $R_{wF} = 0.080$, and ERF = 1.49. A final difference Fourier shows no peaks or holes greater than 0.55 e/Å^3 in any region. The final values of $|F_o|$ and $|F_c|$ for the 3142-reflection 2σ cutoff data set will appear as supplementary material.

Results and Discussion

Local Copper and BPh_4^- Environments. Discrete cationic $[Cu_2(tren)_2X_2]^{2+}$ ($X^- = Cl^-, NCO^-, NCS^-$) and anionic BPh_4^- species are found in the three $[Cu_2(tren)_2X_2](BPh_4)_2$ compounds studied in this paper. The overall structural characteristics for these three compounds are similar to those we recently reported for $[Cu_2(tren)_2(CN)_2](BPh_4)_2$.[8] In Tables II–IV are given the final positional parameters for all of the atoms in $[Cu_2(tren)_2(NCO)_2](BPh_4)_2$, $[Cu_2(tren)_2Cl_2](BPh_4)_2$, and $[Cu_2(tren)_2(NCS)_2](BPh_4)_2$, respectively. It is seen that the small data set for the cyanate has resulted in appreciably larger estimated standard deviations for the atom positions when compared with either the chloride or thiocyanate values. The final anisotropic thermal parameters are listed in Tables V–VII[11] for the cyanate, chloride, and thiocyanate, respectively. The bond distances and angles for $[Cu_2(tren)_2X_2]^{2+}$ and BPh_4^- are summarized in Tables VIII (cyanate), IX (chloride), and X (thiocyanate).

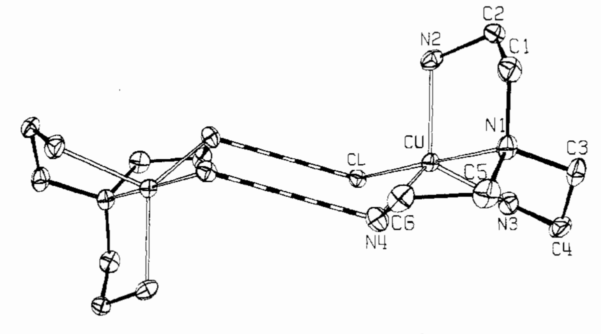

Figure 1. ORTEP plotting of $[Cu_2(tren)_2Cl_2]^{2+}$ indicating the atom numbering; hydrogen atoms are not shown. The metal-ligand bonds are not shaded and the hydrogen bonds are dashed.

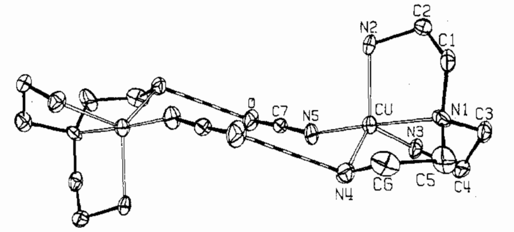

Figure 2. ORTEP plotting of $[Cu_2(tren)_2(NCO)_2]^{2+}$ indicating the atom numbering; hydrogen atoms are not shown. The metal-ligand bonds are not shaded and the hydrogen bonds are dashed.

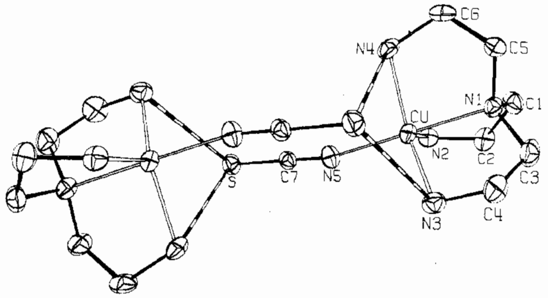

Figure 3. ORTEP plotting of $[Cu_2(tren)_2(NCS)_2]^{2+}$ with atom numbering indicated; hydrogen atoms are not shown. The metal-ligand bonds are not shaded. For each sulfur end of the thiocyanate moieties two possible hydrogen-bonding contacts are indicated.

Figures 1–3 illustrate the structures of the $[Cu_2(tren)_2X_2]^{2+}$ cations in the chloride, cyanate, and thiocyanate compounds, respectively. In each case, the local copper environments are distorted trigonal bipyramids. It would seem, a priori, that for TBP geometry constructed with a tripodal tetradentate ligand like tren the local environment at the copper center would be of C_{3v} symmetry. This is clearly *not* the case for the three Cu(II) systems studied nor for the (tren)Cu–CN$^+$ moiety in $[Cu_2(tren)_2(CN)_2](BPh_4)_2$.[8] In all four cases, the three trigonal-plane angles are ~112, ~120, and ~124°.

At least two cases of regular TBP copper(II) complexes have been reported. The $Cu(NH_3)_2(NCS)_3^-$ moiety in $Cu(NH_3)_2Ag(SCN)_3$ is of regular TBP geometry with the two ammonia groups in the axial positions and the three NCS^- groups in the trigonal plane with Cu–N(NCS^-) = 1.92 Å.[4] The $CuCl_5^{3-}$ ion in $[Cr(NH_3)_6][CuCl_5]$ has been shown[17] to have a crystallographically imposed regular TBP geometry. The $CuCl_5^{3-}$ TBP is axially compressed with $Cu–Cl_{ax} = 2.2964$ (12) Å and $Cu–Cl_{eq} = 2.3912$ (13) Å; it was postulated that

Table II. Final Positional Parameters for All Atoms in $[Cu_2(tren)_2(NCO)_2](BPh_4)_2$,[a] Including Thermal Parameters for All Isotropically Refined Atoms and for All Hydrogen Atoms[b]

Atom	x/a	y/b	z/c	B, Å^2	Atom	x/a	y/b	z/c	B, Å^2
Cu	0.1688 (1)	0.0948 (2)	0.10786 (8)		H(1)	0.049	0.228	0.035	6.54
N(1)	0.2688 (9)	0.237 (1)	0.1280 (8)		H(2)	0.039	0.270	0.107	6.54
N(2)	0.2732 (8)	0.0206 (9)	0.0490 (5)		H(3)	0.113	0.439	0.065	6.58
N(3)	0.1966 (8)	0.044 (1)	0.2060 (6)		H(4)	0.179	0.351	0.026	6.58
N(4)	0.0831 (9)	0.249 (1)	0.0759 (5)		H(5)	0.190	0.382	0.160	8.28
N(5)	0.0726 (8)	−0.028 (1)	0.0911 (6)		H(6)	0.266	0.428	0.114	8.28
C(1)	0.345 (1)	0.219 (2)	0.0835 (8)		H(7)	0.243	−0.022	0.210	6.00
C(2)	0.363 (1)	0.076 (2)	0.0718 (6)		H(8)	0.140	0.016	0.224	6.00
C(3)	0.308 (1)	0.220 (2)	0.196 (1)		H(9)	0.258	0.140	0.280	6.34
C(4)	0.232 (1)	0.160 (2)	0.2370 (7)		H(10)	0.179	0.218	0.240	6.34
C(5)	0.221 (1)	0.365 (2)	0.121 (1)		H(11)	0.363	0.167	0.198	5.91
C(6)	0.148 (2)	0.360 (2)	0.067 (1)		H(12)	0.325	0.302	0.214	5.91
C(7)	0.035 (1)	−0.126 (2)	0.0755 (8)	4.3 (4)	H(13)	0.259	0.042	0.005	4.83
O	−0.0075 (6)	−0.225 (1)	0.0621 (5)		H(14)	0.277	−0.071	0.054	4.83
B	0.735 (1)	0.262 (2)	0.1185 (9)	2.5 (4)	H(15)	0.408	0.065	0.039	5.11
C(11)	0.718 (2)	0.297 (1)	0.0414 (9)		H(16)	0.388	0.035	0.111	5.11
C(12)	0.625 (2)	0.310 (2)	0.013 (1)		H(17)	0.329	0.259	0.043	5.81
C(13)	0.606 (2)	0.322 (2)	−0.054 (2)		H(18)	0.403	0.255	0.103	5.81
C(14)	0.678 (3)	0.322 (2)	−0.095 (1)		H(12b)	0.572	0.310	0.039	5.7
C(15)	0.770 (2)	0.310 (1)	−0.068 (1)		H(13b)	0.543	0.341	−0.074	7.4
C(16)	0.786 (1)	0.297 (1)	−0.001 (1)		H(14b)	0.667	0.320	−0.141	7.2
C(21)	0.655 (1)	0.330 (2)	0.161 (1)		H(15b)	0.852	0.286	0.015	4.9
C(22)	0.623 (1)	0.282 (1)	0.219 (1)		H(16b)	0.820	0.313	−0.097	3.8
C(23)	0.557 (1)	0.346 (2)	0.2570 (8)		H(22b)	0.647	0.202	0.233	4.3
C(24)	0.524 (1)	0.464 (2)	0.239 (1)		H(23b)	0.537	0.299	0.295	4.9
C(25)	0.554 (2)	0.516 (2)	0.184 (1)		H(24b)	0.482	0.506	0.268	4.4
C(26)	0.617 (2)	0.451 (3)	0.1464 (8)		H(25b)	0.528	0.598	0.171	6.0
C(31)	0.835 (1)	0.320 (2)	0.151 (1)		H(26b)	0.634	0.494	0.108	5.3
C(32)	0.878 (2)	0.437 (2)	0.1307 (8)		H(32b)	0.846	0.479	0.093	3.9
C(33)	0.957 (2)	0.491 (2)	0.163 (1)		H(33b)	0.982	0.569	0.145	5.3
C(34)	1.000 (1)	0.433 (2)	0.217 (1)		H(34b)	1.054	0.473	0.238	4.5
C(35)	0.963 (2)	0.317 (2)	0.2389 (9)		H(35b)	0.995	0.282	0.278	4.6
C(36)	0.883 (2)	0.264 (2)	0.207 (1)		H(36b)	0.859	0.187	0.224	4.9
C(41)	0.728 (2)	0.104 (2)	0.1223 (6)		H(42b)	0.579	0.101	0.113	4.0
C(42)	0.635 (1)	0.050 (2)	0.1152 (7)		H(43b)	0.558	−0.121	0.106	5.6
C(43)	0.621 (1)	−0.078 (3)	0.1105 (8)		H(44b)	0.689	−0.254	0.105	5.4
C(44)	0.693 (2)	−0.163 (2)	0.1094 (8)		H(45b)	0.844	−0.167	0.121	5.5
C(45)	0.787 (2)	−0.114 (2)	0.1176 (7)		H(46b)	0.865	0.053	0.124	4.1
C(46)	0.803 (1)	0.016 (2)	0.1223 (7)						

[a] Standard deviations of the least significant digits are in parentheses. The hydrogen atom positions were computed geometrically based upon the positions of the atoms to which they are bound. Tetraphenylborate hydrogens are encoded with the letter b and BPh_4^- atoms are numbered as in ref 19. [b] The hydrogen atoms were given the isotropic temperature factor of the atom to which they are bound. This is the isotropic temperature factor obtained after the last isotropic least-squares refinement.

the axial shortening may be explained by the "stereochemical activity of the 3d electrons".

As would be expected, the TBP local copper(II) environment in $Cu(bpy)_2I^+$ (iodide salt) is distorted.[5] The coordinated iodine is in an equatorial site. It is curious and probably fortuitous that the three trigonal-plane angles for this cation (114, 122, 124°) are similar to those we found for our four $(tren)CuX^+$ ions. However, the distorted TBP geometry reported[18] for the copper centers of the chloride-bridged dimeric cation in $[Cu_2(tet\text{-}b)_2Cl](ClO_4)_3$, where tet-b is *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, also shows similar angles of 115, 121, and 124°. The single chloride bridge is found in an equatorial site. The trigonal-plane angles in this last system must reflect to a certain degree the requirements for folding of the macrocyclic ligand. Some substantiation for this can be seen in the very recently reported[6,19] structure of $[Cu_2([14]\text{-}4,11\text{-diene-}N_4)_2CN](ClO_4)_3$ where two Cu(II) macrocyclic complexes are singly bridged by a CN^- moiety and the trigonal-plane angles at each Cu(II) center are 112, 114, and 135°. In this case, the CN^- bridge also takes an equatorial position.

Finally, the expectations of having local C_{3v} symmetry with a tripodal tetradentate ligand such as tren are borne out in the structure reported[7] for $[Cu(Me_6tren)Br]Br$. The cation is found at a site with C_3 crystallographic symmetry and all three trigonal-plane angles are obviously 120°. The metal–nitrogen distances are $Cu\text{–}N_{eq} = 2.14$ (1) Å and $Cu\text{–}N_{ax} = 2.07$ (1) Å. There is no pairwise association of cations present in $[Cu(Me_6tren)Br]Br$ and it must be concluded that the trigonal-plane distortion that we have found for our four Cu(II) systems results in large part from such a pairwise association.

Further examination of the $[Cu(Me_6tren)Br]^+$ structure points to another interesting aspect of the copper coordination geometry. The copper atom is 0.20 Å (no esd given) out of the trigonal plane toward the Br^- atom. This type of distortion is also to be found in our systems where the copper atom is also out of the plane toward the axial X^- atom. The distances of the copper atoms from the trigonal planes can be calculated to be 0.2569 (7) Å for CN^-, 0.2402 (4) Å for Cl^-, 0.2310 (18) Å for NCO^-, and 0.2216 (8) Å for NCS^-. The larger distances out of the plane appear to be associated with X^- groups that would either be more strongly bonded to copper or have stronger hydrogen-bonding interactions with the other copper center. The hypothesis of the X group pulling the copper atom out of the plane is supported, in part, by noting that the Cu–N(1) bond (i.e., the bond distance to the tertiary tren nitrogen) is longer for the chloride [2.081 (3) Å] and cyanide [2.076 (5) Å] than for either the thiocyanate [2.047 (6) Å] or the cyanate [2.05 (2) Å].

Perusal of Tables VIII–X shows that all of the copper–ligand bond distances are reasonable. The Cu–Cl distance of 2.253 (1) Å is seen to be closer to $Cu\text{–}Cl_{ax}$ than to $Cu\text{–}Cl_{eq}$ for $CuCl_5^{2-}$, as quoted above. The equatorial Cu–Cl distance (2.50 Å) for $[Cu_2(tet\text{-}b)_2Cl](ClO_4)_3$[19] is also to be noted. With

Table III. Final Positional Parameters for All Atoms in $[Cu_2(tren)_2Cl_2(BPh_4)_2]$,[a] Including Isotropic Temperature Factors for Hydrogen Atoms[b]

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c	B, Å^2
Cu	0.15809 (3)	0.06725 (4)	0.09766 (2)	H(1)	0.3793	0.2654	0.0704	5.21
Cl	0.05733 (7)	−0.1063 (1)	0.08968 (5)	H(2)	0.3000	0.2298	0.0145	5.21
N(1)	0.2466 (2)	0.2320 (3)	0.1036 (2)	H(3)	0.4052	0.0589	0.0303	4.23
N(2)	0.2719 (2)	−0.0081 (3)	0.0462 (2)	H(4)	0.3868	0.0538	0.1041	4.23
N(3)	0.1917 (3)	0.0622 (4)	0.2002 (2)	H(5)	0.2984	0.3384	0.1813	4.91
N(4)	0.0525 (2)	0.1942 (3)	0.0574 (2)	H(6)	0.3469	0.2023	0.1794	4.91
C(1)	0.3247 (3)	0.2121 (4)	0.0594 (2)	H(7)	0.2444	0.2013	0.2623	5.99
C(2)	0.3567 (3)	0.0734 (4)	0.0606 (2)	H(8)	0.1576	0.2483	0.2144	5.99
C(3)	0.2870 (3)	0.2469 (4)	0.1730 (2)	H(9)	0.2211	0.4102	0.0639	5.48
C(4)	0.2171 (3)	0.1955 (5)	0.2189 (2)	H(10)	0.1532	0.3807	0.1192	5.48
C(5)	0.1818 (4)	0.3448 (4)	0.0824 (2)	H(11)	0.0574	0.3758	0.0237	5.00
C(6)	0.1026 (3)	0.3045 (4)	0.0321 (2)	H(12)	0.1295	0.2825	−0.0075	5.00
B	0.7377 (3)	0.2923 (4)	0.1181 (2)	H(13)	0.2521	−0.0071	−0.0006	4.67
C(11)	0.7316 (2)	0.1335 (3)	0.1216 (2)	H(14)	0.2843	−0.0967	0.0584	4.67
C(12)	0.6403 (3)	0.0722 (3)	0.1145 (2)	H(15)	0.2469	0.0047	0.2108	5.21
C(13)	0.6285 (3)	−0.0602 (4)	0.1130 (2)	H(16)	0.1375	0.0295	0.2216	5.21
C(14)	0.7087 (3)	−0.1408 (4)	0.1181 (2)	H(17)	0.0106	0.2216	0.0907	4.56
C(15)	0.8006 (3)	−0.0857 (4)	0.1243 (2)	H(18)	0.0119	0.1525	0.0233	4.56
C(16)	0.8113 (3)	0.0489 (3)	0.1258 (2)	H(12b)	0.5831	0.1264	0.1100	3.44
C(21)	0.7080 (2)	0.3259 (3)	0.0402 (2)	H(13b)	0.5638	−0.0972	0.1080	4.14
C(22)	0.6113 (3)	0.3537 (4)	0.0155 (2)	H(14b)	0.7000	−0.2337	0.1169	4.15
C(23)	0.5849 (3)	0.3715 (5)	−0.0505 (2)	H(15b)	0.8593	−0.1402	0.1274	3.99
C(24)	0.6528 (4)	0.3614 (4)	−0.0952 (2)	H(16b)	0.8755	0.0872	0.1299	3.22
C(25)	0.7472 (3)	0.3317 (3)	−0.0740 (2)	H(22b)	0.5630	0.3624	0.0464	3.88
C(26)	0.7741 (3)	0.3159 (3)	−0.0076 (2)	H(23b)	0.5169	0.3895	−0.0645	5.23
C(31)	0.6634 (2)	0.3617 (3)	0.1664 (2)	H(24b)	0.6338	0.3753	−0.1414	4.53
C(32)	0.6309 (3)	0.3035 (3)	0.2220 (2)	H(25b)	0.7964	0.3209	−0.1050	3.76
C(33)	0.5709 (3)	0.3676 (4)	0.2630 (2)	H(26b)	0.8408	0.2983	0.0064	3.31
C(34)	0.5408 (3)	0.4928 (4)	0.2500 (2)	H(32b)	0.6513	0.2165	0.2336	3.83
C(35)	0.5742 (3)	0.5549 (4)	0.1968 (2)	H(33b)	0.5526	0.3237	0.3020	4.43
C(36)	0.6348 (3)	0.4905 (3)	0.1563 (2)	H(34b)	0.4963	0.5351	0.2767	4.25
C(41)	0.8452 (2)	0.3533 (3)	0.1445 (2)	H(35b)	0.5579	0.6440	0.1878	3.95
C(42)	0.8969 (3)	0.3087 (4)	0.2018 (2)	H(36b)	0.6567	0.5364	0.1194	3.23
C(43)	0.9794 (3)	0.3696 (4)	0.2308 (2)	H(42b)	0.8726	0.2310	0.2222	3.35
C(44)	1.0141 (3)	0.4797 (5)	0.2033 (2)	H(43b)	1.0131	0.3358	0.2698	4.48
C(45)	0.9667 (3)	0.5285 (4)	0.1464 (2)	H(44b)	1.0708	0.5249	0.2228	4.90
C(46)	0.8833 (3)	0.4658 (4)	0.1179 (2)	H(45b)	0.9921	0.6041	0.1281	4.85
				H(46b)	0.8506	0.5011	0.0790	3.63

[a] Standard deviations of the least significant digits are in parentheses. The hydrogen atom positions were computed geometrically based upon the positions of the atoms to which they are bound. Tetraphenylborate hydrogens are encoded with the letter b and BPh_4^- atoms are numbered as in ref 19. [b] The hydrogen atoms were given the isotropic temperature factor of the atom to which they are bound. This is the isotropic temperature factor obtained after the last isotropic least-squares refinement.

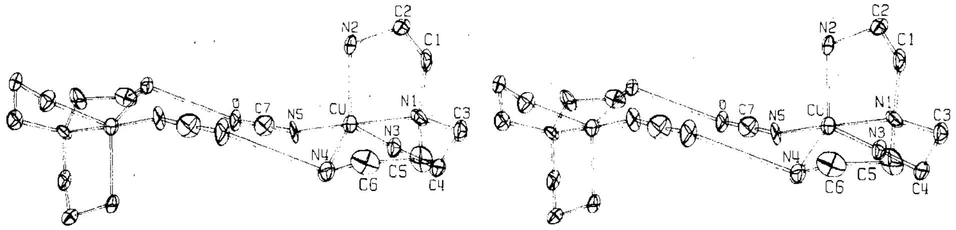

Figure 4. Stereoscopic ORTEP plotting of $[Cu_2(tren)_2(NCO)_2]^{2+}$; the hydrogen atoms are not shown.

respect to the relative bonding tendency of Cu(II) toward either NCO^- or NCS^-, there is an appreciable difference in bond distances: Cu–N(5) = 1.945 (7) Å for NCS^- and Cu–N(5) = 1.87 (2) Å for NCO^-. It would probably be very speculative to try to interpret this difference. The C–N bond distances for either coordinated NCO^- or NCS^- are very close to those for the "free" species.

Least-squares planes were calculated for all of the BPh_4^- phenyl groups of the three compounds and the results are given in Tables XI–XIII,[11] respectively. As expected, all phenyl groups are very planar, and as found for either $[Ni_2(tren)_2(NCO)_2](BPh_4)_2$[20] or $[Cu_2(tren)_2(CN)_2](BPh_4)_2$,[8] the boron atoms are all found to be in the range of 0–0.2 Å out of the phenyl planes. In comparing the BPh_4^- plane orientations in the four $[Cu_2(tren)_2X_2](BPh_4)_2$ structures, one is struck by the configurational mobility of this anion.

Outer-Sphere Association in $[Cu_2(tren)_2X_2]^{2+}$. As is alluded to in the above discussion, we view the $[Cu_2(tren)_2X_2]^{2+}$ units as "outer-sphere" dimers. The magnetic susceptibility evidence for this will be presented in the next section, but first we will take a closer look at the outer-sphere association.

In the four Cu(II) systems (i.e., $X^- = CN^-, Cl^-, NCO^-, NCS^-$) that we have studied with single-crystal X-ray diffraction there are two different outer-sphere associations. The first three $[Cu_2(tren)_2X_2]^{2+}$ dimers all have the same type of outer-sphere association. The stereoscopic view of $[Cu_2(tren)_2(NCO)_2]^{2+}$ illustrated in Figure 4 shows that each NCO^- is nitrogen bonded to one copper atom and at the same time the oxygen atom appears to be hydrogen bonding to nitrogen atom N(4) which is bonded to the second copper atom. If the N(4) nitrogen atom is assumed to be sp^3 hybridized, then the hydrogen atom involved in the hydrogen bond is calculated to be 0.2 Å off the O–N(4) vector. This same type of single-hydrogen-bond contact (per X group) is found for the cyanide and chloride compounds. Furthermore, the X–N(4) distances are quite reasonable for such a hydrogen

Table IV. Final Positional Parameters for All Atoms in $[Cu_2(tren)_2(NCS)_2](BPh_4)_2$,[a] Including Isotropic Temperature Factors for Hydrogen Atoms[b]

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c	B, Å²
Cu	0.15321 (5)	0.09223 (8)	0.10414 (4)	H(1)	0.3184	0.0280	0.2517	6.44
N(1)	0.2506 (4)	0.2362 (6)	0.1321 (3)	H(2)	0.2351	0.1238	0.2477	6.44
N(2)	0.2204 (4)	−0.0178 (6)	0.1815 (3)	H(3)	0.3444	0.2478	0.2124	6.28
N(3)	0.0646 (4)	0.2486 (6)	0.1183 (3)	H(4)	0.3647	0.1306	0.1673	6.28
N(4)	0.2161 (4)	0.0764 (6)	0.0246 (2)	H(5)	0.0855	0.4413	0.1463	7.75
N(5)	0.0620 (4)	−0.0470 (7)	0.0783 (3)	H(6)	0.1183	0.4094	0.0820	7.75
C(1)	0.3155 (5)	0.176 (1)	0.1851 (4)	H(7)	0.2416	0.4378	0.1509	7.48
C(2)	0.2747 (6)	0.0751 (9)	0.2221 (4)	H(8)	0.2055	0.3463	0.2012	7.48
C(3)	0.2073 (7)	0.3560 (9)	0.1551 (5)	H(9)	0.3215	0.1754	−0.0035	7.30
C(4)	0.1157 (7)	0.3756 (8)	0.1253 (5)	H(10)	0.3490	0.0895	0.0579	7.30
C(5)	0.2943 (6)	0.2691 (9)	0.0750 (4)	H(11)	0.3520	0.3106	0.0899	7.13
C(6)	0.3014 (6)	0.150 (1)	0.0359 (4)	H(12)	0.2576	0.3381	0.0899	7.13
C(7)	0.0270 (5)	−0.1501 (8)	0.0643 (3)	H(13)	0.2596	−0.0868	0.1679	5.26
S	−0.0216 (1)	−0.2959 (2)	0.0452 (1)	H(14)	0.1786	−0.0644	0.2044	5.26
B	0.7200 (5)	0.2116 (7)	0.1293 (3)	H(15)	0.0400	0.2315	0.1571	6.32
C(11)	0.7177 (4)	0.0444 (6)	0.1379 (3)	H(16)	0.0159	0.2520	0.0840	6.32
C(12)	0.6393 (4)	−0.0300 (7)	0.1416 (3)	H(17)	0.1772	0.1153	−0.0115	6.12
C(13)	0.6366 (5)	−0.1720 (8)	0.1418 (3)	H(18)	0.2238	−0.0189	0.0152	6.12
C(14)	0.7119 (6)	−0.2472 (7)	0.1381 (3)	H(12b)	0.5830	0.0202	0.1421	4.06
C(15)	0.7916 (5)	−0.1786 (7)	0.1348 (3)	H(13b)	0.5793	−0.2199	0.1442	4.90
C(16)	0.7938 (4)	−0.0366 (6)	0.1348 (3)	H(14b)	0.7110	−0.3470	0.1376	5.33
C(21)	0.7112 (4)	0.2353 (6)	0.0519 (3)	H(15b)	0.8465	−0.2296	0.1324	4.40
C(22)	0.6292 (5)	0.2041 (8)	0.0128 (4)	H(16b)	0.8513	0.0091	0.1324	3.56
C(23)	0.6160 (6)	0.221 (1)	−0.0528 (4)	H(22b)	0.5802	0.1646	0.0321	5.31
C(24)	0.6840 (7)	0.2701 (9)	−0.0813 (4)	H(23b)	0.5578	0.1997	−0.0782	6.38
C(25)	0.7668 (6)	0.2963 (7)	−0.0472 (3)	H(24b)	0.6712	0.2877	−0.1269	5.81
C(26)	0.7794 (5)	0.2802 (7)	0.0185 (3)	H(25b)	0.8161	0.3281	−0.0691	5.25
C(31)	0.6368 (4)	0.2870 (6)	0.1583 (3)	H(26b)	0.8388	0.3015	0.0424	4.23
C(32)	0.6173 (4)	0.2544 (7)	0.2186 (3)	H(32b)	0.6527	0.1842	0.2427	4.37
C(33)	0.5518 (5)	0.3202 (8)	0.2462 (4)	H(33b)	0.5383	0.2895	0.2878	5.17
C(34)	0.5042 (5)	0.4258 (8)	0.2154 (4)	H(34b)	0.4589	0.4752	0.2356	4.45
C(35)	0.5216 (4)	0.4628 (7)	0.1562 (4)	H(35b)	0.4871	0.5376	0.1336	5.31
C(36)	0.5874 (4)	0.3955 (7)	0.1284 (3)	H(36b)	0.5976	0.4234	0.0858	4.71
C(41)	0.8121 (4)	0.2778 (6)	0.1702 (3)	H(42b)	0.8427	0.1235	0.2356	3.91
C(42)	0.8603 (4)	0.2156 (7)	0.2243 (3)	H(43b)	0.9644	0.2371	0.3001	4.72
C(43)	0.9328 (5)	0.2806 (8)	0.2619 (3)	H(44b)	1.0124	0.4529	0.2700	5.01
C(44)	0.9609 (4)	0.4077 (8)	0.2450 (4)	H(45b)	0.9339	0.5610	0.1819	4.74
C(45)	0.9150 (5)	0.4702 (7)	0.1932 (4)	H(46b)	0.8115	0.4567	0.1201	4.12
C(46)	0.8427 (4)	0.4079 (7)	0.1567 (3)					

[a] Standard deviations of the least significant digits are in parentheses. The hydrogen atom positions were computed geometrically based upon the positions of the atoms to which they are bound. Tetraphenylborate hydrogen atoms are encoded with the letter b and BPh_4^- atoms are numbered as in ref 19. [b] The hydrogen atoms were given the isotropic temperature factor of the atom to which they are bound. This is the isotropic temperature factor obtained after the last isotropic least-squares refinement.

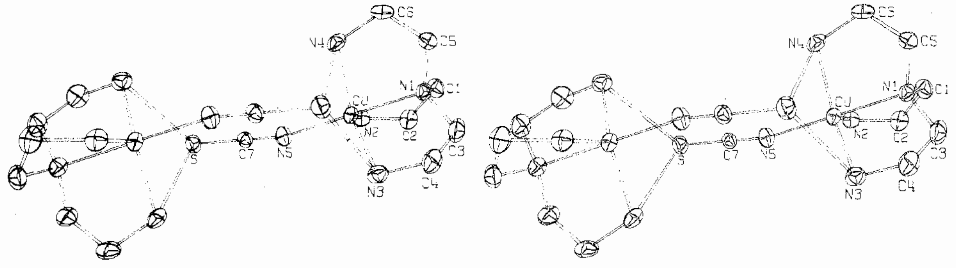

Figure 5. Stereoscopic ORTEP plotting of $[Cu_2(tren)_2(NCS)_2]^{2+}$; the hydrogen atoms are not shown.

bond: cyanate, O–N(4) = 2.94 (2) Å; chloride, Cl–N(4) = 3.368 (4) Å; cyanide, N–N(4) = 3.047 (7) Å.

It is of interest to recall that two different crystalline forms of $[Cu_2(tren)_2(NCO)_2](BPh_4)_2$ have been found.[9] It has been shown that there is an outer-sphere-associated copper dimer present in each case. The copper cyanate dimer described above is present in form I. Form II has not been subjected to X-ray crystallography and one can only speculate as to the structure of the dimeric cation present in form II. However, it is our guess (supportive evidence given later) that the structure of the form II copper cyanate dimer bears some resemblance to that of the outer-sphere dimer present in $[Cu_2(tren)_2(NCS)_2](BPh_4)_2$.

Figure 5 illustrates the structure of $[Cu_2(tren)_2(NCS)_2]^{2+}$. A different type of outer-sphere association is present. The first indicator of this difference came in the early stages of the X-ray work where it was found that the Cu–Cu distance [6.136 (1) Å] in the thiocyanate compound is appreciably shorter than that [6.537 (3) Å] found for the copper cyanate compound. As indicated in Figure 5, the thiocyanate dimer appears to be configured so as to have the thiocyanate sulfur atom involved in hydrogen-bond contacts with two of the nitrogen atoms bonded to the second copper ion. In this case, the hydrogen atoms are not very close to the S–N vectors (0.60 Å for N(3) and 0.46 Å for N(4), assuming tetrahedrally hybridized tren nitrogen atoms) and it might be argued that this is just a close packing of the two $[Cu(tren)(NCS)]^{2+}$ moieties with little hydrogen bonding between them. This more compact structure of $[Cu_2(tren)_2(NCS)_2]^{2+}$ has an effect on the level of electron exchange interaction that is present (vide infra).

In all of the above copper compounds the outer-sphere-

Table VIII. Molecular Distances (Å) and Angles (deg) for $[Cu_2(tren)_2(NCO)_2](BPh_4)_2$[a]

Distances within $[Cu_2(tren)_2(NCO)_2]^{2+}$

Cu–Cu	6.540 (2)	C(1)–C(2)	1.52 (3)
Cu–N(1)	2.06 (1)	C(3)–C(4)	1.53 (3)
Cu–N(2)	2.10 (1)	C(5)–C(6)	1.45 (3)
Cu–N(3)	2.08 (1)	C(2)–N(2)	1.44 (2)
Cu–N(4)	2.08 (1)	C(4)–N(3)	1.43 (2)
Cu–N(5)	1.87 (1)	C(6)–N(4)	1.49 (2)
N(1)–C(1)	1.46 (2)	C(7)–N(5)	1.19 (2)
N(1)–C(3)	1.47 (3)	C(7)–O	1.21 (2)
N(1)–C(5)	1.50 (2)	O–N(4′)	2.95 (1)

Angles within $[Cu_2(tren)_2(NCO)_2]^{2+}$

N(1)–Cu–N(2)	83.5 (5)	N(1)–C(1)–C(2)	111 (1)
N(1)–Cu–N(3)	84.8 (5)	N(1)–C(3)–C(4)	109 (1)
N(1)–Cu–N(4)	83.1 (5)	N(1)–C(5)–C(6)	109 (2)
N(5)–Cu–N(1)	176.7 (6)	C(1)–C(2)–N(2)	107 (1)
N(5)–Cu–N(2)	99.6 (5)	C(3)–C(4)–N(3)	110 (1)
N(5)–Cu–N(3)	95.0 (5)	C(5)–C(6)–N(4)	109 (2)
N(5)–Cu–N(4)	94.3 (5)	C(2)–N(2)–Cu	107.2 (8)
N(2)–Cu–N(3)	111.6 (4)	C(4)–N(3)–Cu	104 (1)
N(2)–Cu–N(4)	120.8 (4)	C(6)–N(4)–Cu	107 (1)
N(3)–Cu–N(4)	124.2 (5)	C(1)–N(1)–C(3)	109 (1)
Cu–N(1)–C(1)	108 (1)	C(1)–N(1)–C(5)	113 (1)
Cu–N(1)–C(3)	108 (1)	C(3)–N(1)–C(5)	110 (1)
Cu–N(1)–C(5)	109 (1)	N(5)–C(7)–O	176 (2)
Cu–N(5)–C(7)	160 (1)	O–N(4′)–Cu′	113.3 (5)

Bond Distances in Tetraphenylborate Anion

C(11)–C(12)	1.39 (4)	C(31)–C(32)	1.43 (3)
C(12)–C(13)	1.37 (4)	C(32)–C(33)	1.36 (3)
C(13)–C(14)	1.35 (4)	C(33)–C(34)	1.37 (4)
C(14)–C(15)	1.37 (5)	C(34)–C(35)	1.40 (3)
C(15)–C(16)	1.37 (4)	C(35)–C(36)	1.37 (3)
C(16)–C(11)	1.35 (3)	C(36)–C(31)	1.41 (3)
C(21)–C(22)	1.38 (3)	C(41)–C(42)	1.41 (3)
C(22)–C(23)	1.41 (3)	C(42)–C(43)	1.35 (4)
C(23)–C(24)	1.36 (4)	C(43)–C(44)	1.35 (3)
C(24)–C(25)	1.35 (4)	C(44)–C(45)	1.42 (4)
C(25)–C(26)	1.38 (3)	C(45)–C(46)	1.37 (3)
C(26)–C(21)	1.39 (3)	C(46)–C(41)	1.39 (3)
B–C(11)	1.62 (3)	B–C(31)	1.63 (3)
B–C(21)	1.62 (3)	B–C(41)	1.64 (3)

Bond Angles in Tetraphenylborate Anion

C(12)–C(11)–C(16)	114 (2)	C(32)–C(31)–C(36)	114 (2)
C(13)–C(12)–C(11)	123 (2)	C(33)–C(32)–C(31)	124 (2)
C(14)–C(13)–C(12)	121 (2)	C(34)–C(33)–C(32)	120 (2)
C(15)–C(14)–C(13)	118 (2)	C(35)–C(34)–C(33)	119 (2)
C(16)–C(15)–C(14)	120 (2)	C(36)–C(35)–C(34)	121 (2)
C(11)–C(16)–C(15)	125 (2)	C(31)–C(36)–C(35)	123 (2)
C(22)–C(21)–C(26)	112 (2)	C(42)–C(41)–C(46)	115 (2)
C(23)–C(22)–C(21)	125 (2)	C(43)–C(42)–C(41)	122 (2)
C(24)–C(23)–C(22)	120 (2)	C(44)–C(43)–C(42)	123 (2)
C(25)–C(24)–C(23)	118 (2)	C(45)–C(44)–C(43)	117 (2)
C(26)–C(25)–C(24)	121 (2)	C(46)–C(45)–C(44)	121 (2)
C(21)–C(26)–C(25)	125 (2)	C(41)–C(46)–C(45)	122 (2)
B–C(11)–C(12)	120 (2)	C(11)–B–C(21)	111 (1)
B–C(11)–C(16)	125 (2)	C(11)–B–C(31)	112 (1)
B–C(21)–C(22)	125 (2)	C(11)–B–C(41)	105 (1)
B–C(21)–C(26)	123 (2)	C(21)–B–C(31)	103 (1)
B–C(31)–C(32)	124 (2)	C(21)–B–C(41)	112 (1)
B–C(31)–C(36)	121 (2)	C(31)–B–C(41)	114 (1)
B–C(41)–C(42)	117 (2)		
B–C(41)–C(46)	127 (2)		

[a] Estimated standard deviations of the least significant figures are given in parentheses.

Table IX. Molecular Distances (Å) and Angles (deg) for $[Cu_2(tren)_2Cl_2](BPh_4)_2$[a]

Distances within $[Cu_2(tren)_2Cl_2]^{2+}$

Cu–Cu	5.7994 (6)	N(1)–C(5)	1.502 (5)
Cu–N(1)	2.081 (3)	C(1)–C(2)	1.492 (6)
Cu–N(2)	2.099 (3)	C(3)–C(4)	1.492 (7)
Cu–N(3)	2.107 (3)	C(5)–C(6)	1.487 (7)
Cu–N(4)	2.066 (3)	C(2)–N(2)	1.441 (5)
Cu–Cl	2.253 (1)	C(4)–N(3)	1.458 (6)
N(1)–C(1)	1.471 (5)	C(6)–N(4)	1.444 (5)
N(1)–C(3)	1.487 (6)	Cl–N(4′)	3.368 (4)
		Cl–H(18′)	2.467 (1)

Angles within $[Cu_2(tren)_2Cl_2]^{2+}$

N(1)–Cu–N(2)	83.0 (1)	C(2)–C(1)–N(1)	110.5 (3)
N(1)–Cu–N(3)	83.4 (1)	C(4)–C(3)–N(1)	110.9 (4)
N(1)–Cu–N(4)	83.8 (1)	C(6)–C(5)–N(1)	111.2 (4)
Cl–Cu–N(1)	177.8 (1)	C(1)–C(2)–N(2)	108.8 (3)
Cl–Cu–N(2)	98.4 (1)	C(3)–C(4)–N(3)	108.7 (4)
Cl–Cu–N(3)	97.7 (1)	C(5)–C(6)–N(4)	108.2 (3)
Cl–Cu–N(4)	94.0 (1)	C(2)–N(2)–Cu	107.5 (2)
N(2)–Cu–N(3)	112.3 (1)	C(4)–N(3)–Cu	105.3 (3)
N(2)–Cu–N(4)	123.8 (1)	C(6)–N(4)–Cu	107.6 (2)
N(3)–Cu–N(4)	119.9 (1)	C(1)–N(1)–C(3)	111.7 (3)
Cu–N(1)–C(1)	107.5 (2)	C(1)–N(1)–C(5)	111.8 (3)
Cu–N(1)–C(3)	107.9 (2)	C(3)–N(1)–C(5)	111.0 (3)
Cu–N(1)–C(5)	106.6 (2)	Cl–N(4′)–Cu′	115.5 (1)

Bond Distances in Tetraphenylborate Anion

C(11)–C(12)	1.396 (5)	C(31)–C(32)	1.389 (5)
C(12)–C(13)	1.372 (5)	C(32)–C(33)	1.388 (6)
C(13)–C(14)	1.371 (6)	C(33)–C(34)	1.372 (6)
C(14)–C(15)	1.375 (6)	C(34)–C(35)	1.372 (6)
C(15)–C(16)	1.393 (5)	C(35)–C(36)	1.387 (5)
C(16)–C(11)	1.392 (5)	C(36)–C(31)	1.392 (5)
C(21)–C(22)	1.404 (5)	C(41)–C(42)	1.394 (5)
C(22)–C(23)	1.380 (6)	C(42)–C(43)	1.380 (5)
C(23)–C(24)	1.361 (6)	C(43)–C(44)	1.367 (6)
C(24)–C(25)	1.362 (6)	C(44)–C(45)	1.378 (7)
C(25)–C(26)	1.386 (5)	C(45)–C(46)	1.394 (6)
C(26)–C(21)	1.389 (5)	C(46)–C(41)	1.397 (5)
B–C(11)	1.638 (5)	B–C(31)	1.640 (5)
B–C(21)	1.646 (5)	B–C(41)	1.648 (5)

Bond Angles in Tetraphenylborate Anion

C(16)–C(11)–C(12)	114.4 (3)	C(36)–C(31)–C(32)	115.3 (3)
C(11)–C(12)–C(13)	123.6 (3)	C(31)–C(32)–C(33)	122.3 (3)
C(12)–C(13)–C(14)	120.5 (4)	C(32)–C(33)–C(34)	120.8 (4)
C(13)–C(14)–C(15)	118.5 (4)	C(33)–C(34)–C(35)	118.5 (4)
C(14)–C(15)–C(16)	120.4 (4)	C(34)–C(35)–C(36)	120.3 (4)
C(15)–C(16)–C(11)	122.7 (4)	C(35)–C(36)–C(31)	122.8 (3)
C(26)–C(21)–C(22)	114.4 (3)	C(46)–C(41)–C(42)	114.8 (3)
C(21)–C(22)–C(23)	122.6 (4)	C(41)–C(42)–C(43)	123.4 (3)
C(22)–C(23)–C(24)	120.6 (4)	C(42)–C(43)–C(44)	119.9 (4)
C(23)–C(24)–C(25)	119.1 (4)	C(43)–C(44)–C(45)	119.6 (4)
C(24)–C(25)–C(26)	120.3 (4)	C(44)–C(45)–C(46)	119.6 (4)
C(25)–C(26)–C(21)	123.0 (3)	C(45)–C(46)–C(41)	122.7 (4)
C(11)–B–C(21)	104.1 (3)	C(12)–C(11)–B	119.6 (3)
C(11)–B–C(31)	111.8 (3)	C(16)–C(11)–B	125.7 (3)
C(11)–B–C(41)	114.4 (3)	C(22)–C(21)–B	122.5 (3)
C(21)–B–C(31)	112.1 (3)	C(26)–C(21)–B	122.8 (3)
C(21)–B–C(41)	112.2 (3)	C(32)–C(31)–B	124.2 (3)
C(31)–B–C(41)	102.6 (3)	C(36)–C(31)–B	120.4 (3)
		C(42)–C(41)–B	121.7 (3)
		C(46)–C(41)–B	122.7 (3)

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

associated dimeric cations are magnetically isolated by the rather large tetraphenylborate anions. Since we will next describe the *intradimer* electron exchange for the series of copper compounds, a closer look at the packing in a typical unit cell is called for. Figure 6 illustrates the packing of dimeric $[Cu_2(tren)_2Cl_2]^{2+}$ cations and BPh_4^- anions. Interactions between two copper ions in different outer-sphere dimers is prevented by phenyl groups that are shielding in many directions. There does *not* appear to be any viable pathway for an appreciable electron exchange between outer-sphere dimers. The closest Cu–Cu approach between outer-sphere dimers is 9.40 Å. The packing is similar for the other three copper systems where the closest interdimer Cu–Cu approaches are as follows: cyanate, 10.78 Å; cyanide, 10.89 Å; thiocyanate, 11.21 Å.

Intradimer Electron Exchange. Variable-temperature magnetic susceptibility data have already been reported[6,9] for the copper cyanide, thiocyanate, and cyanate (forms I and II)

Table X. Molecular Distances (Å) and Angles (deg) for $[Cu_2(tren)_2(NCS)_2](BPh_4)_2$[a]

Distances within $[Cu_2(tren)_2(NCS)_2]^{2+}$			
Cu–Cu	6.136 (1)	C(1)–C(2)	1.45 (1)
Cu–N(1)	2.047 (6)	C(3)–C(4)	1.43 (1)
Cu–N(2)	2.088 (6)	C(5)–C(6)	1.44 (1)
Cu–N(3)	2.075 (6)	C(2)–N(2)	1.42 (1)
Cu–N(4)	2.060 (5)	C(4)–N(3)	1.45 (1)
Cu–N(5)	1.946 (7)	C(6)–N(4)	1.45 (1)
		C(7)–N(5)	1.15 (1)
N(1)–C(1)	1.49 (1)	C(7)–S	1.622 (8)
N(1)–C(3)	1.46 (1)	S–N(3′)	3.463 (6)
N(1)–C(5)	1.50 (1)	S–N(4′)	3.736 (7)
Angles within $[Cu_2(tren)_2(NCS)_2]^{2+}$			
N(1)–Cu–N(2)	83.6 (2)	N(1)–C(1)–C(2)	113.3 (7)
N(1)–Cu–N(3)	84.0 (2)	N(1)–C(3)–C(4)	113.8 (8)
N(1)–Cu–N(4)	84.0 (2)	N(1)–C(5)–C(6)	111.9 (7)
N(5)–Cu–N(1)	179.0 (2)	C(1)–C(2)–N(2)	110.9 (7)
N(5)–Cu–N(2)	95.5 (2)	C(3)–C(4)–N(3)	112.7 (8)
N(5)–Cu–N(3)	96.8 (3)	C(5)–C(6)–N(4)	110.7 (7)
N(5)–Cu–N(4)	96.1 (3)	C(2)–N(2)–Cu	108.1 (5)
N(2)–Cu–N(3)	120.4 (2)	C(4)–N(3)–Cu	107.7 (5)
N(2)–Cu–N(4)	112.3 (2)	C(6)–N(4)–Cu	109.2 (5)
N(3)–Cu–N(4)	123.8 (2)	C(1)–N(1)–C(3)	109.6 (6)
Cu–N(1)–C(1)	107.7 (4)	C(1)–N(1)–C(5)	112.3 (6)
Cu–N(1)–C(3)	108.4 (5)	C(3)–N(1)–C(5)	111.7 (6)
Cu–N(1)–C(5)	107.0 (4)	N(5)–C(7)–S	179.3 (7)
Cu–N(5)–C(7)	162.7 (6)	S–N(3′)–Cu′	88.7 (2)
		S–N(4′)–Cu′	50.9 (1)
Bond Distances in Tetraphenylborate Anion			
C(11)–C(12)	1.394 (9)	C(31)–C(32)	1.394 (9)
C(12)–C(13)	1.39 (1)	C(32)–C(33)	1.38 (1)
C(13)–C(14)	1.36 (1)	C(33)–C(34)	1.36 (1)
C(14)–C(15)	1.38 (1)	C(34)–C(35)	1.37 (1)
C(15)–C(16)	1.39 (1)	C(35)–C(36)	1.39 (1)
C(16)–C(11)	1.396 (9)	C(36)–C(31)	1.388 (9)
C(21)–C(22)	1.41 (1)	C(41)–C(42)	1.398 (9)
C(22)–C(23)	1.39 (1)	C(42)–C(43)	1.40 (1)
C(23)–C(24)	1.35 (1)	C(43)–C(44)	1.38 (1)
C(24)–C(25)	1.36 (1)	C(44)–C(45)	1.35 (1)
C(25)–C(26)	1.39 (1)	C(45)–C(46)	1.37 (1)
C(26)–C(21)	1.399 (9)	C(46)–C(41)	1.395 (9)
B–C(11)	1.644 (9)	B–C(31)	1.645 (9)
B–C(21)	1.646 (9)	B–C(41)	1.646 (9)
Bond Angles in the Tetraphenylborate Anion			
C(12)–C(11)–C(16)	114.1 (5)	C(32)–C(31)–C(36)	115.0 (6)
C(11)–C(12)–C(13)	123.1 (6)	C(31)–C(32)–C(33)	123.2 (6)
C(12)–C(13)–C(14)	121.0 (7)	C(32)–C(33)–C(34)	120.2 (7)
C(13)–C(14)–C(15)	118.2 (7)	C(33)–C(34)–C(35)	118.8 (7)
C(14)–C(15)–C(16)	120.4 (6)	C(34)–C(35)–C(36)	120.8 (7)
C(15)–C(16)–C(11)	123.2 (6)	C(35)–C(36)–C(31)	122.0 (6)
C(22)–C(21)–C(26)	114.2 (6)	C(42)–C(41)–C(46)	114.8 (5)
C(21)–C(22)–C(23)	122.9 (7)	C(41)–C(42)–C(43)	122.0 (6)
C(22)–C(23)–C(24)	119.5 (8)	C(42)–C(43)–C(44)	120.2 (7)
C(23)–C(24)–C(25)	121.2 (8)	C(43)–C(44)–C(45)	118.8 (7)
C(24)–C(25)–C(26)	119.0 (7)	C(44)–C(45)–C(46)	121.2 (7)
C(25)–C(26)–C(21)	123.1 (6)	C(45)–C(46)–C(41)	122.9 (6)
B–C(11)–C(12)	123.7 (5)	C(11)–B–C(21)	104.5 (5)
B–C(11)–C(16)	121.8 (5)	C(11)–B–C(31)	112.0 (5)
B–C(21)–C(22)	119.2 (6)	C(11)–B–C(41)	111.2 (5)
B–C(21)–C(26)	126.6 (6)	C(21)–B–C(31)	111.2 (5)
B–C(31)–C(32)	121.2 (5)	C(21)–B–C(41)	113.8 (5)
B–C(31)–C(36)	123.5 (5)	C(31)–B–C(41)	104.4 (5)
B–C(41)–C(42)	123.3 (5)		
B–C(41)–C(46)	121.6 (5)		

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

Table XIV. Exchange Parameters for the $[Cu_2(tren)_2X_2](BPh_4)_2$ Compounds

X^-	J, cm^{-1}	X^-		J, cm^{-1}
Br^-	−3.5	NCO^-	form I[a]	0.09–0.16[b]
Cl^-	−3.2		form II[a]	0.05–0.06[b]
CN^-	−1.8	NCS^-		0.05–0.07[b]
OH^-	−2.1			

[a] There are two crystalline forms of $[Cu_2(tren)_2(NCO)_2](BPH_4)_2$; see ref 9. [b] These are values of $|J|$ and are determined with EPR;[9] $|J|$ varies with temperature from the smaller value at 345°K to the larger value at 95°K.

compounds. In the first case, an antiferromagnetic interaction was found with $J = -1.8$ cm^{-1} ($\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$). The other three compounds did not show any signs of interactions down to 4.2°K. However, for these three compounds, it was possible to determine an exchange parameter J using EPR. In each case, weak singlet-to-triplet state EPR transitions were observed and from their magnetic field positions, it is easy to calculate values of $|J|$. The exchange parameters are summarized in Table XIV. From the structural characteristics of form I of $[Cu_2(tren)_2(NCO)_2](BPh_4)_2$, it is to be anticipated[9] that the electron-exchange interaction is antiferromagnetic; i.e., the J value is negative. It may well be that the exchange interaction is ferromagnetic for form II of Cu–NCO and for the Cu–NCS compound. This possibility grows out of the more angular bonding interaction present, for instance, at the sulfur end of the thiocyanate "bridge".

The variable-temperature susceptibilities of $[Cu_2(tren)_2Cl_2](BPh_4)_2$, $[Cu_2(tren)_2Br_2](BPh_4)_2$, and $[Cu_2(tren)_2(OH)_2](BPh_4)_2$ have been measured and there is an antiferromagnetic interaction present in each compound. Figure 7 shows that, in the case of $[Cu_2(tren)_2Br_2](BPh_4)_2$, there is a maximum in the susceptibility at ~6.5°K and the effective magnetic moment goes from 1.94 BM at 296°K to 1.03 BM at 4.2°K. The data are given in Table XV[11] (chloride and bromide) and Table XVI[11] (hydroxide). In the case of the chloride compound there is a susceptibility maximum at ~5.5°K and the μ_{eff} goes down to 1.13 BM at 4.2°K from 2.01 BM at 296°K. The hydroxide compound does not have a maximum in susceptibility above 4.2°K; however, the μ_{eff} is 1.30 BM at 4.2°K and 1.99 BM at 296°K. The data for these three compounds have been fit to the Bleaney–Bowers copper dimer equation with a simplex minimization routine.[13] In each case, three parameters were used: a g value, an exchange parameter J, and a Curie–Weiss constant Θ. The resultant parameters are given in Tables XV and XVI.[11] The Cu–Br compound has $J = -3.5$ cm^{-1}, and the Cu–Cl compound $J = -3.2$ cm^{-1}, while for the Cu–OH compound $J = -2.1$ cm^{-1}. In summary, Table XIV shows that in this series of copper outer-sphere dimers the J values encompass a range of some two orders of magnitude. It should be added that this series of J values taken together, in conjunction with the *relatively* large magnitude of some of the J values, is additional evidence in support of the proposal that we are studying *intradimer* exchange interactions. Before we turn to the most important point of relating the above exchange work to anion-assistance effects seen in solution redox processes, three other points need be mentioned.

The presence of outer-sphere dimers in $[Cu_2(tren)_2(OH)_2](BPh_4)_2$ and $[Cu_2(tren)_2Br_2](BPh_4)_2$ is substantiated, in part, by the above susceptibility data as well as considerable additional data. In short, the infrared and electronic absorption spectra clearly support the isostructural nature of the Cu–OH and Cu–Br compounds. For example, the Q-band EPR spectra of the Cu–Cl and Cu–Br compounds, shown in Figure 8, compare favorably and show that the copper ions in $[Cu_2(tren)_2Br_2](BPh_4)_2$ are trigonal bipyramidal. Thus, in the case of a trigonal bipyramidal copper ion the d_{z^2} ground state leads to $g_\parallel$ values close to 2.00.

With the structures of the Cu–NCO (form I) and Cu–NCS compounds in hand, it is now possible to rationalize the observed[9] temperature dependences of the exchange parameters seen for these two compounds as well as that observed for the Cu–NCO (form II) compound. For the Cu–NCO (form I) compound $|J| = 0.09$ cm^{-1} at 345°K, whereas, at 95°K, the

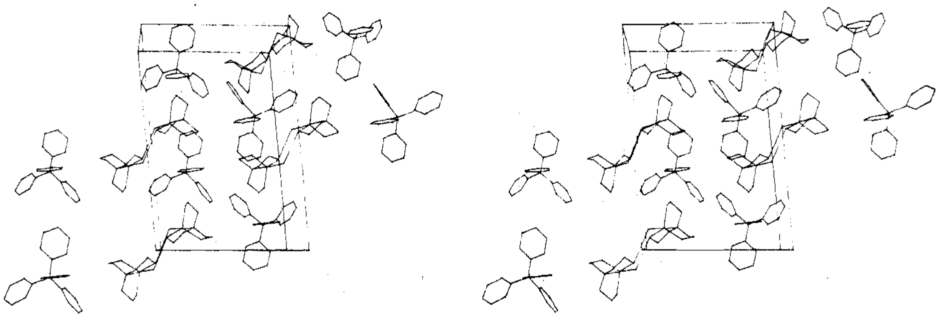

Figure 6. Stereoscopic packing diagram of $[Cu_2(tren)_2Cl_2](BPh_4)_2$; hydrogen atoms are not shown.

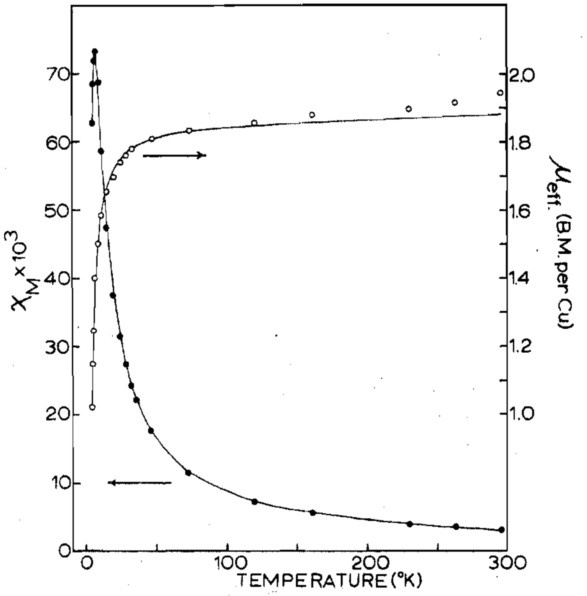

Figure 7. Corrected molar paramagnetic susceptibility (χ_M in cgsu) and effective magnetic moment per Cu(II) (μ_{eff} in BM) as a funtion of temperature for $[Cu_2(tren)_2Br_2](BPh_4)_2$. The solid lines are least-squares-fit theoretical lines where $J = -3.5$ cm^{-1}, $g = 2.13$, and $\Theta = 0.36°$.

value of $|J|$ is 0.16 cm^{-1}. This pronounced temperature dependence can be explained by recalling that for this compound there are single hydrogen-bond contacts involving the oxygen end of the cyanate and it would seem that the contraction of the crystal in the range of 345–95°K could be "absorbed" in large part by dimensional changes associated with the hydrogen bonds. Compression of the two hydrogen bonds at the lower temperature could give the larger J value of 0.16 cm^{-1}. The more compact structure of the $[Cu_2(tren)_2(NCS)_2]^{2+}$ dimer probably does not allow as great a change in dimensions, and, consequently, for $[Cu_2(tren)_2(NCS)_2](BPh_4)_2$ at 345°K $|J| = 0.05$ cm^{-1}, which changes little to a value of $|J| = 0.07$ cm^{-1} at 95°K. It is of interest to note that for Cu–NCO (form II) $|J| = 0.05$ cm^{-1} at 345°K and $|J| = 0.06$ cm^{-1} at 95°K, a temperature dependence which could be taken to indicate that the structure of this form of the copper cyanate compound is similar to that of the thiocyanate compound.

In the above discussion, it is implied that the *intradimer* electron exchange interaction is propagated by the electron density associated with the hydrogen bonds. A nitrogen-deuterated sample of form I of the Cu–NCO compound was prepared, i.e., $[Cu_2(tren\text{-}d_6)_2(NCO)_2](BPh_4)_2$. The X-band spectra (345–95°K) of this deuterated compound show that the J value is, within experimental error, the *same* as found for the protonated compound. This is to a certain degree unexpected, in light of both common sense and the studies of Meisenheimer and Swalen[21] where they found for $HCrO_2$ and $DCrO_2$ a difference in J of about 25% (smaller for $DCrO_2$).

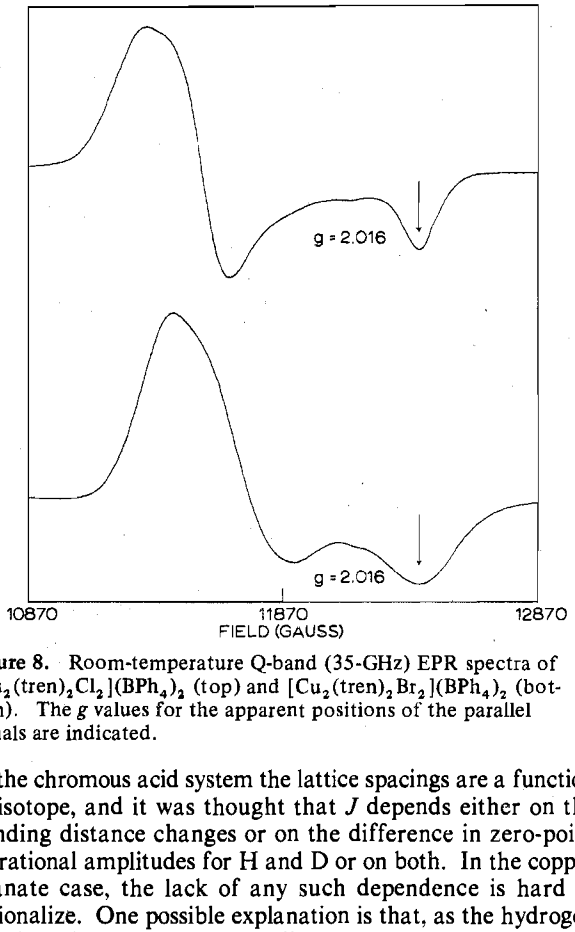

Figure 8. Room-temperature Q-band (35-GHz) EPR spectra of $[Cu_2(tren)_2Cl_2](BPh_4)_2$ (top) and $[Cu_2(tren)_2Br_2](BPh_4)_2$ (bottom). The g values for the apparent positions of the parallel signals are indicated.

In the chromous acid system the lattice spacings are a function of isotope, and it was thought that J depends either on the bonding distance changes or on the difference in zero-point vibrational amplitudes for H and D or on both. In the copper cyanate case, the lack of any such dependence is hard to rationalize. One possible explanation is that, as the hydrogen that is active in hydrogen bonding is not exactly on the N–O axis, it may be that, when a deuterium atom is substituted, the small changes in distance, if any, are accompanied by changes in N–H(D)···O angle so that the net overlap in the system is independent of isotope. No matter what electron density is propagating the *intradimer* exchange interaction, the X anion in $[Cu_2(tren)_2X_2](BPh_4)_2$ does dramatically modulate the interaction level.

Exchange Effects in Outer-Sphere Redox Precursors. The electron exchange interactions in the above series of copper outer-sphere dimers are weak; however, because the interactions exceed the copper hyperfine interaction, the electrons on the two copper centers are exchanging at an appreciable rate (greater than $\sim 10^{10}$ sec^{-1}). Thus, the outer-sphere association provides an effective pathway for electron transfer. The question at hand is whether the electron exchange effects that we see for the *solid* samples of Cu(II) outer-sphere dimers can give any insight into "anion assistance" effects seen[22] for outer-sphere redox processes in *solution.*

In solution an outer-sphere redox reaction between two transition metal complexes can be viewed as a two-step process.

Initially, an outer-sphere binuclear precursor is formed. In the second step electron transfer occurs between the two metal centers. *If the precursor is relatively long-lived, the rate of intraprecursor electron transfer is important in determining the observed rate of the redox process.* It should be noted that in Marcus' treatment of outer-sphere redox rates, it is assumed that the intraprecursor electron transfer is fast and as such does *not* affect the overall rate.[23] Cannon and Gardiner[24] reported the first measurement of the lifetime (~10 sec) of a precursor complex. Their precursor was formed in the reaction of $[(NH_3)_5Co^{III}LH_2]^{2+}$, where $L^{3-} = N(CH_2COO)_3{}^{3-}$, with iron(II). The specific rate constant for intramolecular electron transfer was determined as 0.115 ± 0.004 sec^{-1}. The precursor complex in this case is inner sphere bridged and it was necessary to speculate as to the structural details of the species involved in the intramolecular electron transfer. Four other papers reporting the measurement of intramolecular electron transfer in *inner*-sphere-associated precursors have appeared recently.[25-28] There has been only one report[29] of a determination of the rate of "intramolecular" electron transfer for an *outer*-sphere redox process in solution. The first-order rate constant (0.19 sec^{-1}) for electron transfer was measured for an outer-sphere precursor formed in solution from $Co(NH_3)_5(H_2O)^{3+}$ and $Fe(CN)_6{}^{4-}$. There was no discussion of the structural characteristics of this outer-sphere-associated precursor. It would, of course, be interesting to know the pathway of electron transfer in such a precursor.

If anion assistance effects seen in outer-sphere solution redox processes grow out of variable electron transfer rates in precursors (certainly there are other explanations), then the $[Cu_2(tren)_2X_2](BPh_4)_2$ compounds give insight into such an effect. The outer-sphere association in these solids can be characterized structurally and the two copper ions provide a means of monitoring the inter-metal-ion electron exchange interaction. There is, obviously, no difference in oxidation states of the two copper centers in these outer-sphere dimers. Consequently, there is no net electron transfer from one copper to the other; however, there can be, under the conditions of an appreciable exchange interaction, an electron exchange between the two copper centers.

Perhaps a specific example would clarify the above discussion. The rate of the outer-sphere redox reaction between $Co(NH_3)_6{}^{3+}$ and aqueous V^{2+} is dramatically affected by the anion in solution.[22] For example, relative to chloride, the thiocyanate anion enhances the rate of this reaction such that $k_{NCS}/k_{Cl} = 1.0 \times 10^3$. It appears that the anion binds to the labile V^{2+} to give the aqueous species VCl^+ or $VNCS^+$, respectively. These, then, react with the cobalt complex to give an outer-sphere precursor which probably involves some degree of hydrogen bonding, viz., $(NH_3)_5Co(H_2N{-}H)\cdots Cl{-}V^+$. If this precursor is relatively long-lived, then the facility with which electrons transfer through the outer-sphere bridge will be important. Under these conditions the "anion assistance" effect is understandable in that the anion plays a major role in determining the viability of the outer-sphere "bridge" for electron transfer.

The electron exchange interaction in the $[Cu_2(tren)_2X_2](BPh_4)_2$ compounds is gauged by an effective spin Hamiltonian of the form $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$. Even though there are no unpaired electrons on the Co(III) center in the above $(NH_3)_5CoH_2N{-}H\cdots Cl{-}V^+$ intermediate, exchange-type interactions can partly determine the rate of electron transfer through the outer-sphere bridge. This becomes clear as we review what the $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$ Hamiltonian represents. The "real" Hamiltonian corresponding to this effective exchange Hamiltonian would contain kinetic energy terms and electron–nuclear and electron–electron potential energy terms for *all* electrons of the system as well as nuclear–nuclear repulsion terms.[30] Thus, the effective exchange Hamiltonian is an attempt, for a system with unpaired electrons on two metal centers, to account for all of these energy terms with an exchange parameter *J*. With our definition of the Hamiltonian, $2J$ is the energy separation between the triplet and singlet electronic states of a two-metal system with one unpaired electron on each metal center. The exchange parameter can be shown with certain approximations to be a function of exchange, Coulomb, and overlap integrals.[30,31] The formalism of $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$ cannot be used for the interactions that lead to electron transfer in $[(NH_3)_5Co^{III}H_2N{-}H\cdots Cl{-}V^{II}]^+$, but they certainly are "exchange-type" interactions. In other words, the rate of electron transfer between the V^{II} center and the Co^{III} center is set by the difference in energy and level of interaction between the two electronic states of the system, i.e., $[(NH_3)_5Co^{III}H_2N{-}H\cdots Cl{-}V^{II}]^+$ and $[(NH_3)_5Co^{II}H_2N{-}H\cdots Cl{-}V^{III}]^+$.

It should be possible to construct many different types of outer-sphere associations with copper dimers and efforts are under way to do this to check the viability of various outer-sphere pathways for electron transfer.

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Registry No. $[Cu_2(tren)_2Br_2](BPh_4)_2$, 55748-25-9; $[Cu_2(tren)_2Cl_2](BPh_4)_2$, 55748-23-7; $[Cu_2(tren)_2(CN)_2](BPh_4)_2$, 51464-43-8; $[Cu_2(tren)_2(OH)_2](BPh_4)_2$, 54750-19-5; $[Cu_2(tren)_2(NCO)_2](BPh_4)_2$, 52699-44-2; $[Cu_2(tren)_2(NCS)_2](BPh_4)_2$, 52665-52-8.

Supplementary Material Available. Tables of the final values of $|F_o|$ and $|F_c|$ will appear following these pages in the microfilm edition of this journal for the following compounds: $[Cu_2(tren)_2Cl_2](BPh_4)_2$, 3527 reflections; $[Cu_2(tren)_2(NCO)_2](BPh_4)_2$, 1212 reflections; $[Cu_2(tren)_2(NCS)_2](BPh_4)_2$, 3142 reflections. Tables I, V–VII, XI–XIII, XV, and XVI, showing analytical data, anisotropic thermal parameters, least-squares planes, and susceptibility data, will also appear following these pages. 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 Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC40747C-10-75.

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Crystal and Molecular Structure of 2,2'-Bis[1-thia-*closo*-decaborane(8)], 2,2'-(1-B_9H_8S)$_2$

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The crystal and molecular structure of 2,2'-bis[1-thia-*closo*-decaborane(8)] was determined by single-crystal X-ray diffraction techniques. The crystals form in the monoclinic space group $P2_1/n$ with $a = 12.184$ (4), $b = 9.777$ (3), and $c = 6.601$ (1) Å with $\beta = 95.72$ (2)°, and $Z = 2$. The conventional R index converged at 0.0437 with full-matrix least-squares refinement including the overall scale factor, all positional parameters and all anisotropic temperature factors for nonhydrogen atoms, and isotropic temperature factors for the hydrogen atoms. The molecule has $C_i(\bar{1})$ space group imposed point symmetry; the center of inversion of the molecule is at the midpoint of a B–B bond [1.678 (5) Å] joining the two bicapped square antiprism frameworks of the B_9H_8S moieties. The sulfur atom is in an "axial" position and the equatorial belt of four boron atoms closest to the sulfur atom contains the boron through which the B_9H_8S units are connected. The average B–S distance is 1.923 (3) Å. The B–B distances of the cage range from 1.940 (3) to 1.689 (4) Å.

Introduction

The vacuum pyrolysis of thiadecaborane(11) produces three isomers of $(B_9H_8S)_2$ in about 5% yield.[1,2] As described previously, ^{11}B NMR cannot distinguish between two of the possible isomers, 2,2'-(1-B_9H_8S)$_2$ and 6,6'-(1-B_9H_8S)$_2$.[1] An X-ray structural study was initiated to elucidate the structure of one of these isomers. It was also realized that a definitive location of the B–B bond linking the two B_9H_8S moieties would allow assignment of the NMR for $(B_9H_8S)_2$ molecules and extrapolation of these results to the parent molecule, 1-B_9H_9S, and many of its derivatives. Subsequent to completion of the crystallographic study certain structural features of the molecule were found to correlate with known reaction chemistry of 1-B_9H_9S.

Experimental Section

Collection and Reduction of the X-Ray Diffraction Data. The synthesis, separation, and spectral properties of (1-B_9H_8S)$_2$ thiaboranes have been described previously.[1] Single crystals (mp 159.5–161.0° uncor, sealed capillary) of 2,2'-(1-B_9H_8S)$_2$ were obtained by gradual evaporation of solvent from a CH_2Cl_2 solution of pure 2,2'-(1-B_9H_8S)$_2$.

The crystal used for the X-ray diffraction work was a rather irregular trapezoidal plate with parallel sides, altitude, and thickness of ca. 0.18, 0.27, 0.20, and 0.11 mm, respectively. The crystal was mounted with the a axis (direct space) approximately parallel to the glass fiber (spindle axis).

Precession photographs gave approximate cell dimensions, indicated $2/m$ (C_{2h}) Laue symmetry, and exhibited the systematic absences $0k0$ for $k = 2n + 1$ and $h0l$ for $h + l = 2n + 1$, consistent only with the centrosymmetric space group $P2_1/n$.

The density of another crystal was determined to be 1.66 g cm^{-3} using the flotation method in aqueous KCl; the calculated value is 1.167 g cm^{-3} for two $(B_9H_8S)_2$ molecules per unit cell. In this space group this requires that the center of symmetry of each molecule resides at a special position.

Table I. Experimental Data for the X-Ray Diffraction Study of 2,2'-(1-B_9H_8S)$_2$

(a) Crystal Parameters

$a = 12.184$ (4) Å	Space group $P2_1/n$
$b = 9.777$ (3) Å	Mol wt 275.02
$c = 6.601$ (1) Å	ρ(obsd) = 1.166 g cm^{-3}
$\beta = 95.72$ (2)°	ρ(calcd) = 1.167 g cm^{-3}
$V = 782.4$ (4) Å^3	2 molecules/unit cell

(b) Intensity Measurements

Reflections measd: hkl for $h, k > 0$; $0kl$ for $l > 0$
Maximum 2θ: 118.6°
Radiation: Cu Kα
Scan speed: 2.0–24.0°/min
Standard background counts were taken at the beginning and end of each 2θ scan
Scan mode: θ(crystal)–2θ(counter)
Three standard reflections measured after every 36 reflections, no decay observed, no unusual deviation in intensity
1140 reflections collected, plus 82 systematically extinct

The crystal from which the precession photographs were obtained was transferred to an arcless goniometer head on a Syntex $P\bar{1}$ autodiffractometer equipped with graphite-monochromatized Cu Kα radiation. After centering and orientation, 2θ, ω, and χ settings for 15 different reflections were accurately determined. The Syntex least-squares routine gave the unit cell dimensions listed in Table I. Intensity data were then collected on magnetic tape. Specifics of the intensity measurements are given in Table 1. No absorption corrections were made. The linear absorption coefficient for Cu Kα radiation was estimated to be 26.25 cm^{-1}.

Solution and Refinement of the Structure. Programs used in determining the structure included DATRDN, NORMSF, FC, FOURR, LOADAT, BONDLA, and LISTFC from ref 3. The least-squares structure refinement program used was CLS written by Schilling.[4] The thermal ellipsoid drawing was obtained by use of ORTEP, by Johnson,[5] and ORFFE, by Busing, Martin, and Levy,[5] was used for bond distances, angles, and errors.

Scattering factors for neutral boron and sulfur were taken from ref 6, and the values of Stewart, Davidson, and Simpson were used for hydrogen.[7] The function minimized during least-squares refinement was $\sum w \| F_o| - |F_c\|^2$ where $w = \sigma^{-2}$ for the appropriate F_o. The residual discrepancy term used was defined in the usual manner, i.e., $R_F = \sum \| F_o| - |F_c\| / \sum |F_o|$.

Following data reduction in which Lorentz and polarization corrections were made, an origin-removed Patterson map was determined. The position of the sulfur atom was easily determined and using only this atom a structure factor calculation was made using