

C(3). This is the most staggered conformation obtainable. The apparent implication of this difference in rotational configuration is that the barrier to rotation about the Fe–N bond is not very high, with crystal packing forces having a major influence on the configuration adopted in the crystal.

Fluxionality of $\text{Fe}(\text{CO})_4\text{C}_5\text{H}_5\text{N}$. It is well known that scrambling of axial and equatorial CO groups occurs rapidly in $\text{Fe}(\text{CO})_5$, even at -170° .¹¹ It occurred to us that the presence of one ligand distinctly differing from CO in its σ -donor and π -acceptor properties, such as an amine, might introduce a barrier to this process (assumed, generally, to proceed through the Berry pseudorotation pathway) sufficient to allow observation of a slow exchange ^{13}C spectrum. The reasoning was that the strong σ -donor and virtually nonexistent π -acceptor capacities of pyridine might create such a marked preference for it to occupy an axial site in the trigonal bipyramid, that passage through a trigonal bipyramidal intermediate having pyridine in an equatorial site might be strongly disfavored. Detailed inspection of equatorial–axial exchange of CO groups in an $\text{Fe}(\text{CO})_4\text{L}$ type molecule by means of the Berry process necessitates such an intermediate. How-

(11) J. P. Jesson and P. Meakin, *J. Amer. Chem. Soc.*, **95**, 1344 (1973).

ever, the ^{13}C nmr spectrum of 20% enriched $\text{Fe}(\text{CO})_4\text{C}_5\text{H}_5\text{N}$ is a single sharp line at all temperatures down to *ca.* -100° . Of course, it is still possible that the slow exchange spectrum—or at least a broadening of the line—might be observed at still lower temperature, but the available cryostat could not be operated at lower temperatures.

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Supplementary Material Available. Tables containing the observed and calculated structure amplitudes and the principle axes of the vibrational ellipsoids of both compounds 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 \$5.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-3438.

Electronic and Crystallographic Study of Two Cyanide-Bridged Copper(II) Dimers. Magnetic Exchange Interactions through a Linear Cu–CN–Cu Bridge and a Hydrogen-Bonded Cu–CN···H–N–Cu System

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Abstract: The single-crystal X-ray structures of $[\text{Cu}_2([14]4,11\text{-diene-N}_4)_2\text{CN}](\text{ClO}_4)_3$, where $[14]4,11\text{-diene-N}_4$ is 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene, and $[\text{Cu}_2(\text{tren})_2(\text{CN})_2](\text{BPh}_4)_2$, where $\text{tren} = 2,2',2''\text{-triaminotriethylamine}$, have been determined and preliminary results communicated. The copper atom environments are trigonal bipyramidal in both of these Cu(II) dimers; in the former complex there is Cu–CN–Cu bridging while in the latter system bridging is *via* the coordinated cyanide on each copper atom hydrogen bonding through its N atom to a primary amine of the tren ligand coordinated to the second Cu atom, Cu–CN···HN–Cu. The electronic structures of the two Cu(II) dimers have been characterized by electronic absorption, ir, esr, and variable-temperature (4.2–283°K) magnetic susceptibility measurements. Low-intensity $\nu(\text{CN})$ bands are shown to be indicative of CN bridging for these two Cu(II) dimers. Antiferromagnetic exchange is present in both cyanide-bridged dimers, where $J = -4.8 \text{ cm}^{-1}$ for the Cu–CN–Cu system and $J = -1.8 \text{ cm}^{-1}$ for the Cu–CN···HN–Cu system. The observed exchange in the hydrogen-bonded tren system is of special interest, because it provides a lucid illustration of magnetic exchange through a bridging moiety possessing only σ -electron density. The observed electronic effects are discussed with regard to the coordination geometry and bridge bonding in each molecule, and a comparison is made between the two cyanide-bridged systems and the five-coordinate chloride-bridged compound $[\text{Cu}_2(\text{tet-b})_2\text{Cl}](\text{ClO}_4)_3$, where $(\text{tet-b}) = \text{rac-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane}$. The magnetism ($J = -144 \text{ cm}^{-1}$) for this system is reported in this paper.

The bonding and spectroscopic properties of a considerable number of transition metal complexes with coordinated cyanide have been studied. Although

there are many known and characterized polymeric systems,³ there is a paucity of reports on metal dimers with cyanide bridging. In the case of Cu(II), this is probably due to the low inherent stability in aqueous

(1) Esso Fellow, 1971–1972; Mobil Fellow, 1972–1973.

(2) Camille and Henry Dreyfus Fellow, 1972–1977.

(3) D. F. Shriver, *Struct. Bonding*, **1**, 32 (1966).

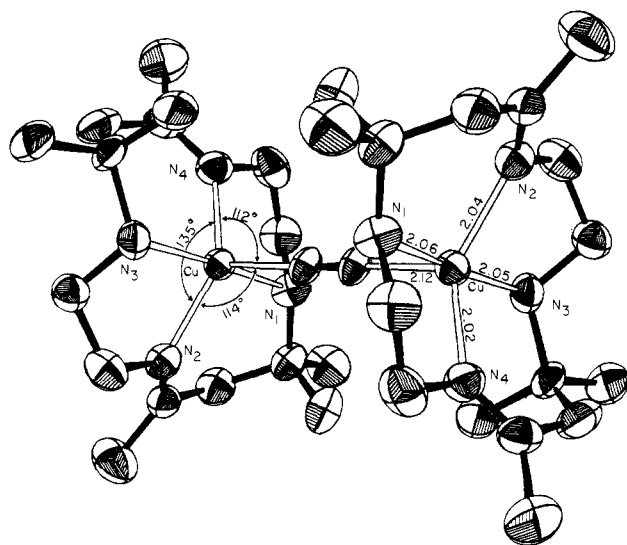


Figure 1. Molecular structure of the dimeric cation $[\text{Cu}_2([\text{14}]4,11\text{-diene-N}_4)_2\text{CN}](\text{ClO}_4)_3$. The singly bridging cyanide anion is left unlabeled in that the carbon and nitrogen atoms cannot be distinguished. All intraligand bonds are shaded and the copper trigonal plane angles are indicated.

solution of Cu(II) in the presence of cyanide.⁴ In fact, the first stable Cu(II) cyanide complex was reported as recently as 1966.⁵ To date, there has been no report of a crystallographic characterization of a cyanide-bridged transition metal dimer or cluster complex. However, such complexes have been claimed on the basis of infrared data.⁶⁻⁷ Only room-temperature magnetic susceptibility measurements have been carried out on the purportedly cyanide-bridged metal dimers.⁵ In this paper we report the molecular structures and physical properties of two cyanide-bridged Cu(II) dimers.

Two markedly different and interesting modes of cyanide bridging are illustrated by these two Cu(II) dimers, and, as such, a characterization of the electronic structure of both systems is important. Electronic properties mainly reflecting the coordination environment about the individual Cu(II) centers were investigated using electronic absorption and esr techniques as discussed previously in the literature,⁸⁻¹¹ whereas variable-temperature (4.2–283°K) magnetic susceptibility and esr techniques were used to study the physical properties resulting from the electron exchange interaction between the Cu(II) centers in a dimer unit. In addition, a discussion of the cyanide infrared spectra of these two authenticated Cu(II) dimers is presented in order to illustrate a procedure that is different from the usual frequency analysis for the detection of cyanide bridging.

Results and Discussion

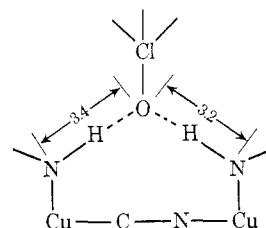
Molecular Structures. The X-ray crystal structures

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of both $[\text{Cu}_2([\text{14}]4,11\text{-diene-N}_4)_2\text{CN}](\text{ClO}_4)_3$,¹² where $[\text{14}]4,11\text{-diene-N}_4$ is 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene, and $[\text{Cu}_2(\text{tren})_2(\text{CN})_2](\text{BPh}_4)_2$,¹³ where $\text{tren} = 2,2',2''\text{-triaminotriethylamine}$, have been determined in this work, and this section will serve as a preliminary communication of the results.

The monocyanide crystallizes in the space group $C2/c$ with dimensions $a = 24.040$ (8), $b = 15.062$ (5), $c = 12.525$ (4) Å, and $\beta = 98.50$ (2)°. The measured and calculated densities are $\rho_{\text{meas}} = 1.47$ (3), and $\rho_{\text{calcd}} = 1.50$ g cm⁻³ ($Z = 4$, mol wt = 1012). Intensity data were taken on a computer-controlled Picker four-circle diffractometer to $2\theta = 45^\circ$, including 2941 reflections in total, of which 2138 were considered observed reflections. The structure was solved by standard heavy atom Patterson and Fourier methods to an agreement of $R_{\text{WF}} = 0.053$ and $R_{\text{F}} = 0.074$ (all data used). All thermal motions were taken as being anisotropic and all hydrogen atoms were included at their calculated positions using a bond length of 0.95 Å. An absorption correction was made.

The structure of the cation $[\text{Cu}_2([\text{14}]4,11\text{-diene-N}_4)_2\text{CN}]^{3+}$ is depicted in Figure 1. The two copper atoms are bridged by a single cyanide group; the molecule is located on a center of inversion, and only unique distances are given. Unfortunately, in the crystal the cyanide group is disordered so that the carbon and nitrogen ends cannot be distinguished. Pseudoatoms are shown in the figure with the Cu–X distance indicated. The coordination geometry about the copper atoms can be seen to be a distorted trigonal bipyramid. It is important to note that the thermal ellipsoids for the atoms about the Cu atom are not excessive with a maximum mean square displacement of 0.27 Å². Because there is static disorder, this means that the geometries about the two different Cu atom centers (*i.e.*, the Cu atom bonded as Cu–CN and the other bonded as Cu–NC) are almost identical. Two other features of the coordination spheres of the copper atoms are worthy of mention. First, the axial (N_1 and N_3) ligands demonstrate an elongation over the equatorial ligands. Second, the equatorial plane is distorted greatly from trigonal symmetry, one angle larger and two smaller than 120°. In this compound the two metal-containing moieties are bridged in a more remote fashion by two of the three perchlorate counterions through hydrogen bonds to ligand nitrogens in the following fashion



Because the perchlorate oxygens have large thermal vibrations, it is difficult to ascertain accurate contact distances; however, the best values obtained are indicated in the above drawing.

The compound $[\text{Cu}_2(\text{tren})_2(\text{CN})_2](\text{BPh}_4)_2$ crystallizes in the $P2_1/c$ space group with $a = 13.792$ (7), $b =$

- (12) R. G. Jungst and G. D. Stucky, unpublished results.
- (13) D. M. Duggan and D. N. Hendrickson, unpublished results.

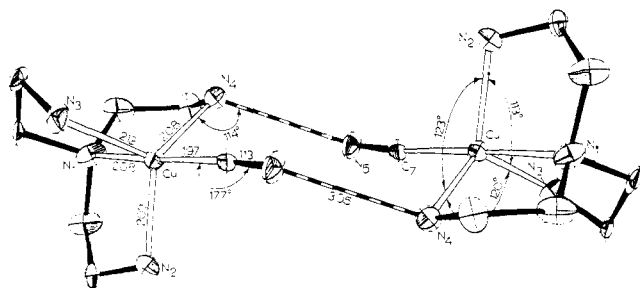


Figure 2. Molecular structure of the dimeric cation in $[\text{Cu}_2(\text{tren})_2(\text{CN})_2](\text{BPh}_4)_2$ with the two hydrogen-bonding interactions indicated by dashed lines and the tren (2,2',2''-triaminotriethylamine) intraligand bonds shaded. The trigonal plane angles for the copper trigonal bipyramid are indicated.

10.338 (6), $c = 20.316$ (14) Å, and $\beta = 94.27^\circ$. Using $Z = 4$ and mol wt = 1177, the calculated density ρ_{calcd} is 1.28 g cm^{-3} , which compares favorably with the measured value $\rho_{\text{measd}} = 1.26$ (2) g cm^{-3} . Data for this system were collected and treated as described for the first system, refinement of 2773 total reflections corrected for absorption with an anisotropic model with all hydrogen atoms having progressed to a weighted $R_{\text{wF}} = 0.047$ and $R_{\text{F}} = 0.065$. The structural features of the dimer $[\text{Cu}_2(\text{tren})_2(\text{CN})_2]^{2+}$ are shown in Figure 2, where distances on only half of the molecule are given because the dimer is located on a center of inversion in the unit cell. Hydrogen atoms are not shown in Figure 2. The two halves of the dimer are bridged solely by means of two $\text{N}-\text{H}\cdots\text{N}$ hydrogen-bonding contacts between a cyanide nitrogen atom and a tren ligand. Although the bridging hydrogen atom cannot be seen, its position can be calculated from the $\text{M}-\text{N}-\text{C}$ (tren) angle to be ~ 0.05 Å from the $\text{N}-\text{N}$ vector. The 3.05 Å $\text{N}-\text{N}$ distance is similar to that observed for most $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds.¹⁴ The possibility in transition metal complexes of hydrogen-bond formation between the nitrogen end of a coordinated cyanide ion and a coordinated amine has not been given much importance in the past. Very recently the X-ray crystal structure of a five-coordinate copper(II) molecule was reported¹⁵ where polymeric chains are formed by chloride ion hydrogen bond bridges to the secondary nitrogen atoms on pairs of monomers.

Contrary to the case for $[\text{Cu}_2([\text{14}]\text{4,11-diene-N}_4)_2\text{CN}](\text{ClO}_4)_3$, the cyanide ligands in $[\text{Cu}_2(\text{tren})_2(\text{CN})_2](\text{BPh}_4)_2$ occupy axial positions in the trigonal bipyramidal environment about the copper atoms, leading to an axially compressed structure. In addition, the equatorial ligands are *not* arranged in perfect threefold symmetry. An equatorial distortion is also present in the monocyanide dimer; however, in $[\text{Cu}_2(\text{tren})_2(\text{CN})_2](\text{BPh}_4)_2$ there are two large equatorial angles and one small angle whereas in the monocyanide system there are two small and one large.

The structure¹⁶ of the chloride bridged $[\text{Cu}_2(\text{tet-b})_2\text{Cl}](\text{ClO}_4)_3$ to which we shall refer later in this paper is illustrated in Figure 3. While the dimer contains hy-

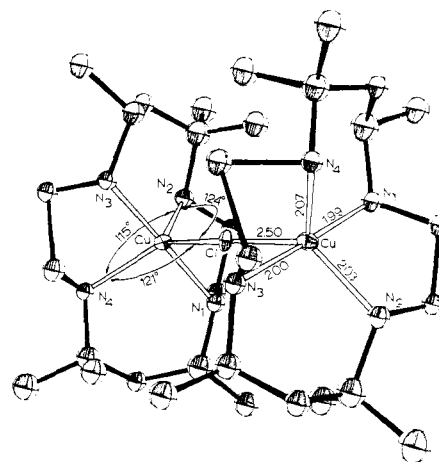


Figure 3. Molecular structure of the dimeric cation in $[\text{Cu}_2(\text{tet-b})_2\text{Cl}](\text{ClO}_4)_3$ (drawing made from data reported in ref 16). The (tet-b) intraligand bonds are shaded and the copper trigonal plane angles are indicated.

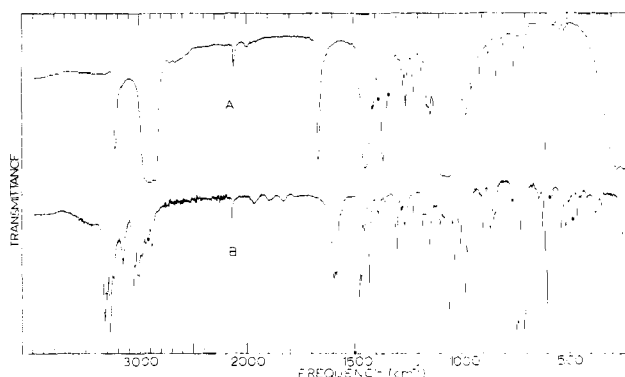


Figure 4. Infrared spectra of (A) $[\text{Cu}_2([\text{14}]\text{4,11-diene-N}_4)_2\text{CN}](\text{ClO}_4)_3$ and (B) $\text{Cu}_2(\text{tren})_2(\text{CN})_2(\text{BPh}_4)_2$, the samples being prepared as Nujol and KBr pellet, respectively.

drogen-bonded perchlorate anions as in the cyanide case, these have been left out of the figure and are not considered an important part of the structure in the present context. The chloride is located 2.50 Å from each copper atom and is bonded to each in an equatorial site of the trigonal bipyramid. It is notable that the two copper skeletons of this system are mutually skewed as befits the molecule's location on a crystallographic twofold rotation axis. This is in contrast to the alignment observed for the cyanide systems, both of which contain a center of inversion.

Infrared and Electronic Spectra. The ir spectra of $[\text{Cu}_2([\text{14}]\text{4,11-diene-N}_4)_2\text{CN}](\text{ClO}_4)_3$ and $[\text{Cu}_2(\text{tren})_2(\text{CN})_2](\text{BPh}_4)_2$ are reproduced in Figure 4. Both compounds were run pelleted in KBr; however, in the case of the monocyanide-bridged compound, spectral changes were seen over what is present in a Nujol mull spectrum, and as such we report the Nujol mull spectrum for this compound. The cyanide stretching vibrations fall at 2130 and 2140 cm^{-1} , respectively, in the two compounds. The work of Dows, *et al.*,¹⁷ indicated that, with the assumption of similar bond strengths for both terminally bound and bridging cyanide systems, the $\nu(\text{CN})$ frequency should be signifi-

(14) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman, San Francisco, Calif., 1960; W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, New York, N. Y., 1968.

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(17) D. A. Dows, A. Haim, and W. K. Wilmarth, *J. Org. Nucl. Chem.*, 21, 33 (1961).

cantly greater for the bridging case than for the terminal one. Frequency regions have since been established for the various types of cyanide binding. Both of the cyanide-bridged copper dimers reported in this work have cyanide stretching frequencies which are in the region characteristic of bridging systems. In some cases,¹⁸ the decrease in $\nu(\text{CN})$ upon dissolution has been taken as indicative of bridging in the solid state, and a similar conclusion has been drawn from a frequency decrease upon reaction of dimethylgold cyanide with triphenylphosphine.⁷ For the dicyanide-bridged system, the solution $\nu(\text{CN})$ band is decreased in frequency by $\sim 30\text{--}40\text{ cm}^{-1}$ from the solid-state value (molecular weight measurements indicate an essentially monomeric species in acetonitrile solution), and the $-\text{CN}-$ bridged nature of the solid-state structure thus evidenced. Since the monocyano complex is highly associated in acetonitrile (mol wt_{eff} = 338) solution, the changes in the infrared spectrum are not easily interpreted. The most interesting observation that we have made in respect to the cyanide stretching vibration in our two complexes relates to the *intensity* of the cyanide bands. The $\nu(\text{CN})$ band in the dicyanide-bridged system is *weak* in the solid state relative to the *strong* band seen in the solution spectra. The relatively low intensity of the solid-state $\nu(\text{CN})$ band is evident in Figure 4, where it is possible to compare them to other modes in the compounds. We must conclude that upon binding both ends of the CN^- group the intensity of the cyanide stretch decreases. This decrease in intensity is observable even for the hydrogen-bonded system where the bonding is certainly very weak. The only requirement is, of course, that the bridging interaction decrease the charge gradient along the C-N axis so that the dipole moment derivative for the vibrational mode is much smaller. While it is *not* our purpose to review all cyanide ir data in order to investigate the generality of the cyanide band intensity criteria, it is suggested that this phenomena be investigated in future and even past work.

Electronic absorption spectra (visible region) were recorded for $[\text{Cu}_2(\text{tren})_2(\text{CN})_2](\text{BPh}_4)_2$ and $[\text{Cu}_2(\text{tet-b})_2\text{Cl}](\text{ClO}_4)_3$ pelleted in KBr and for a Nujol mull of $[\text{Cu}_2([14]4,11\text{-diene-N}_4)_2\text{CN}](\text{ClO}_4)_3$. The results are given in Table I. There are several trigonal bipyra-

Table I. Electronic Spectral Data^a

Compound	\AA	kK	Intensity
$[\text{Cu}]_2(\text{tren})_2(\text{CN})_2(\text{BPh}_4)_2$	5940	16.84	m w
	7530	13.28	s, v br
	8710	11.5	m (sh)
$[\text{Cu}_2([14]4,11\text{-diene-N}_4)_2\text{CN}](\text{ClO}_4)_3$	6140	16.29	m
	7360	13.59	s
	9500	10.5	m (sh)
	6000 ^b	16.7	m (sh)
$[\text{Cu}_2(\text{tet-b})_2\text{Cl}](\text{ClO}_4)_3$	6670	14.99	s
	8310	12.03	m

^a Obtained from samples pelleted in KBr. ^b Only detectable as an asymmetry on the 6670- \AA peak.

midal copper(II) systems known and in some cases, e.g., $[\text{Cu}(\text{tren})(\text{NCS})]\text{SCN}$,¹¹ two features are seen in the visible spectrum, while in other cases three features are resolved. The unpaired electron in a copper(II)

(18) D. Cooper and R. A. Plane, *Inorg. Chem.*, **5**, 2209 (1966).

trigonal bipyramidal complex is in the " d_{z^2} " (from now on quotation marks signifying "ideally" will be omitted but implicitly assumed to apply to all orbital designations) orbital (z axis is threefold axis), which in D_{3h} symmetry gives a ${}^2A'$ ground state. Transitions are possible (still D_{3h} symmetry) to the ${}^2E'$ ($d_{x^2-y^2}$, d_{xy}) and ${}^2E''$ (d_{xz} , d_{yz}) excited states, crystal field theory predicting that the ${}^2A' \rightarrow {}^2E''$ band will be at higher energy. The appearance of more than two bands in various trigonal bipyramidal complexes has been accounted for by distortions splitting the degenerate excited states and/or spin-orbit splitting. For example, single-crystal polarized spectra have been obtained for D_{3h} symmetry in $\text{Cu}(\text{NH}_3)_2\text{Ag}(\text{SCN})_3$, and an assignment was given for the three peaks.¹⁹ In this system the two highest energy features are assigned to transitions to the spin-orbit split ${}^2E'$, and the third band is assigned to the only allowed transition from the ${}^2\Gamma_9$ component of the spin-orbit split ${}^2E''$ state. A similar study¹⁹ has been made for the distorted trigonal bipyramidal complex $[\text{Cu}(\text{bipy})_2]\text{I}$. It is notable that for these two systems the ${}^2E'$ excited state (d_{xy} , $d_{x^2-y^2}$) lies at higher energy than the ${}^2E''$ state, a fact attributed to the presence of out-of-plane π -bonding with the three equatorial NCS^- in one case and the one equatorial I^- in the other case.

The three dimeric copper complexes under study in this paper do have distorted trigonal bipyramidal structures, and perusal of Table I shows that each exhibits three features in the visible region. Without polarization data the assignment of the features cannot be definitive. For the $[\text{Cu}_2(\text{tren})_2(\text{CN})_2](\text{BPh}_4)_2$ case the coordination approximates threefold symmetry, with the strongest ligand, $-\text{C}\equiv\text{N}$, in the axial position. In the absence of π bonding with the cyanide, the ordering of states will be ${}^2A'(d_{z^2}) < {}^2E'(d_{x^2-y^2}, d_{xy}) < {}^2E''(d_{xz}, d_{yz})$. Thus the two band system centered at 12.4 kK would be assigned to the ${}^2A' \rightarrow {}^2E'$ transitions, where the ${}^2E'$ state is split *via* spin-orbit coupling and low-symmetry crystal field components. The low-symmetry contribution is probably small in this case; the theoretical splitting due to the spin-orbit effect is 2λ (free ion) $\cong 1.65\text{ kK}$,¹⁹ which is close to the observed value (due to the poor resolution the band splitting cannot be measured accurately). The higher energy band in this system would then be assigned to the only electronically allowed transition to the spin-orbit split ${}^2E''$ components, ${}^2\Gamma_8(A') \rightarrow {}^2\Gamma_9(E'')$.

Electronic spectral assignments are more difficult to make for the two equatorially bridged systems due to the probable electronic distortion from threefold axial symmetry. For the chloride compound the closest two bands are 1.65 kK apart and these lie highest in energy with the third lying 3.0 kK lower. Contrary to the previously described dicyanide system, one might speculate here that it is the split ${}^2E'$ state that lies highest, as proposed for $[\text{Cu}(\text{bipy})_2]\text{I}$.²⁰ If the complex were monomeric this assignment could be checked by looking for the higher g_{\perp} value (see esr section). The spectrum may also arise from the ${}^2E'$ lying lower and being split by both spin-orbit coupling and low symmetry to a total of 3.0 kK.

(19) B. J. Hathaway, D. E. Billing, R. J. Dudley, R. J. Fereday, and A. A. G. Tomlinson, *J. Chem. Soc. A*, 806 (1970).

(20) A. D. Toy, M. D. Hobday, P. D. W. Boyd, T. D. Smith, and J. R. Pilbrow, *J. Chem. Soc. Dalton Trans.*, 1259 (1973).

In the single-CN bridged species there are three distinguishable bands which are separated by 3.1 and 2.7 kK. It is clear here that a low-symmetry component must be proposed to account for this splitting, independent of which pair of bands are associated with ${}^2E'$.

Electron Spin Resonance. X-Band and Q-band esr spectra were run for powder samples of $[\text{Cu}_2(\text{tren})_2(\text{CN})_2](\text{BPh}_4)_2$, $[\text{Cu}([14]4,11\text{-diene-N}_4)_2\text{CN}](\text{ClO}_4)_3$, and $[\text{Cu}_2(\text{tet-b})_2\text{Cl}](\text{ClO}_4)_3$; reproductions of the Q-band spectra of all three compounds appear in Figure 5. Previous to discussing each spectrum, a brief review of the theoretical expectations for a purely trigonal bipyramidal structure will be given. The ${}^2A_1'$ ground state (D_{3h} symmetry assumed) is spin-orbit coupled to the ${}^2E''$ (d_{xz}, d_{y^2}) excited state, resulting in the expressions $g_{\perp} = 2(1 - 3k^2\lambda/\Delta_2)$ and $g_{\parallel} = 2.00$ (2.0023 with the relativistic correction). The parameter Δ_2 is the ligand field splitting between the ${}^2A_1'$ ground state and the ${}^2E''$ excited state, while k is an orbital reduction factor and λ (-829 cm^{-1}) is the free ion spin-orbit coupling constant. While it is found that $g_{\perp} > g_{\parallel}$ for trigonal bipyramidal copper systems, g_{\parallel} values have been found as large as 2.08, which has been interpreted by Slade, *et al.*,¹¹ as being due to distortion from ideal threefold symmetry.

The X-band powder spectrum of $[\text{Cu}_2(\text{tren})_2(\text{CN})_2](\text{BPh}_4)_2$ was found to exhibit one fairly isotropic signal, while the Q-band spectrum shown in Figure 5 is typical of what is expected for a trigonal bipyramidal copper center, with $g_{\parallel} = 2.006$ and $g_{\perp} = 2.134$. In fact, if Δ_2 is taken as $16,800 \text{ cm}^{-1}$ as assigned above, a k value of 0.68 is required to give $g_{\perp} = 2.134$. This k value does not seem unreasonable, although it is not a sensitive function of the band assignment. We note with surprise the apparent simplicity of the Q-band spectrum. The work of Smith and coworkers^{20,21} has indicated that for copper ions interacting in pairs a complicated spectrum may arise. References 20 and 21 describe the treatment of a copper dimer where the principal g -tensor axes of each copper center are colinear (a required condition if the molecule possesses a center of inversion), and yet there is no g axis parallel to the copper-copper vector. In these circumstances the zero-field splitting tensor will not be coincident with the g tensor of the dimer, and as a result off-axis extrema may appear which give rise to additional features in a multicrystalline esr spectrum. Such complications have been noted in the esr spectra of some copper complexes.²² The fact that for $[\text{Cu}_2(\text{tren})_2(\text{CN})_2](\text{BPh}_4)_2$ the threefold symmetry axis of each copper (taken as the g_{\parallel} direction) makes an angle of 44° with respect to the Cu-Cu vector, and yet the spectrum is typical of only a single center, leads to the conclusion that for $d_{\text{Cu-Cu}} = 6.1 \text{ \AA}$ the elements of the zero-field splitting tensor are too small to be of detectable importance in this regard.

The Q-band spectrum of $[\text{Cu}_2(\text{tet-b})_2\text{Cl}](\text{ClO}_4)_3$ (shown in Figure 5) is simple in appearance but probably profoundly complex in origin. A nearly isotropic derivative ($g = 2.087$) is seen where the low-field lobe is broadened somewhat. Chao and Lunsford²³ have

(21) P. D. W. Boyd, A. D. Toy, T. D. Smith, and J. R. Pilbrow, *J. Chem. Soc. Dalton Trans.*, 1549 (1973).

(22) D. M. Duggan and D. N. Hendrickson, submitted for publication.

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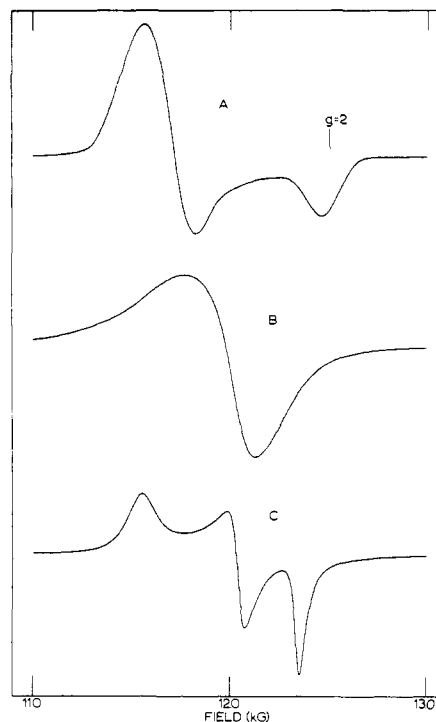


Figure 5. Q-Band (35.0 GHz) powder esr spectra of (A) $[\text{Cu}_2(\text{tren})_2(\text{CN})_2](\text{BPh}_4)_2$, (B) $[\text{Cu}_2(\text{tet-b})_2\text{Cl}](\text{ClO}_4)_3$, and (C) $[\text{Cu}_2([14]4,11\text{-diene-N}_4)_2\text{CN}](\text{ClO}_4)_3$.

shown in a simple treatment that for exchange coupled dimer systems where the two g tensors are not colinear, it is possible to observe only an isotropic spectrum even though the individual tensors are of axial or even lower symmetry. The crystal structure of $[\text{Cu}_2(\text{tet-b})_2\text{Cl}](\text{ClO}_4)_3$ shows (Figure 3) that the pseudothreefold symmetry axes of the two Cu atoms include an angle of 68° . This angle may quite reasonably be expected to lead to an isotropic spectrum, considering the large exchange integral (see next section) between the copper atoms.

The spectral consequences of zero-field splitting between copper atoms with g -tensor elements misaligned by 90° has been treated quantitatively by Smith and coworkers.^{24,25} They have found that complicated spectra may be expected. Therefore, it seems clear that for the single-Cl-bridged copper dimer under consideration here, where the g tensors are mutually skewed, there is a large exchange coupling and there are zero-field splitting contributions from both dipolar coupling and pseudodipolar (excited-state exchange) effects; the spectral results are presently uninterpretable on a quantitative basis. It does appear that the overriding effect is the exchange averaging in that the spectrum is so close to isotropic.

The esr spectrum of the mono-CN-bridged complex illustrates yet another unexpected result. It consists of three g values (2.183, 2.096, and 2.041), which at first glance would seem to be indicative of a copper g tensor with rhombic symmetry (*i.e.*, $g_{xx} \neq g_{yy} \neq g_{zz}$). However, we must consider several aspects of the crystalline structure of $[\text{Cu}_2([14]4,11\text{-diene-N}_4)_2\text{CN}](\text{ClO}_4)_3$ before

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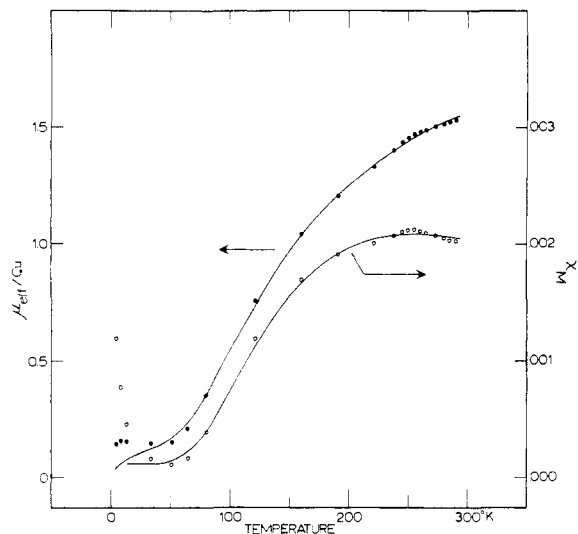


Figure 6. The effective moment per copper (μ_{eff} in BM) vs. temperature and corrected molar paramagnetic susceptibility vs. temperature curves for $[\text{Cu}_2(\text{tet-b})_2\text{Cl}](\text{ClO}_4)_3$. The solid lines are least-squares fit theoretical lines (see Table II for fitting parameters).

trying to rationalize the spectrum. As seen in Figure 1 the trigonal axes of the copper ions are parallel to each other (the molecule sits on a center of inversion) and make an angle of $\sim 90^\circ$ with the Cu–Cu vector. One would thus expect to observe for this system a spectrum undistorted by $\bar{D} - \bar{g}$ tensor misalignment. But it must be realized that there is a crystallographic disordering of the dimer about its “center of symmetry;” that is the dimer is turned opposite directions in every other unit cell of the crystal. Although it can be seen from the thermal parameters of the refined atoms the basic geometries of the two ends of the dimer must be quite similar, the fact remains that one end has $\text{Cu}-\text{N}_4\text{C}\equiv\text{N}$ coordination while the other is $\text{Cu}-\text{N}_4\text{N}\equiv\text{C}$. One effect that might result from this difference in coordination is that the g tensors will be misaligned somewhat, in spite of the apparently close structural alignment. While the distortion of a dimer spectrum due to g tensor misalignment by a *general* angle has never been calculated, there is the possibility that the apparent three g value spectrum we observe could be due to such an effect.

Another interpretation of the single-CN-system esr spectrum might be that the g values of the two halves of the dimer are different due to the difference between $\text{Cu}-\text{C}\equiv\text{N}$ and $\text{Cu}-\text{N}\equiv\text{C}$ bonding and that the observed spectrum results from an overlap of two axial spectra. The 5-cm^{-1} exchange (*vide infra*) between the two halves of the dimer would tend to average any distinction between them, however, and on this basis we cannot suggest this simple explanation as the correct one. Also the electronic spectrum of the system shows three peaks as discussed previously and shows no sign of the complication that two greatly different electronic structures would produce. Among the various possible explanations discussed none can be supported fully until detailed single-crystal studies are completed or until the spectrum can be computer simulated with an allowance for g tensor misalignment (a sufficiently general program is presently unavailable).

Magnetic Susceptibility. Magnetic susceptibility

measurements from 290 to 4.2°K have been made for the three copper dimers in this study: the monocyano-bridged, the monochloride-bridged, and the hydrogen-bonded dicyano-bridged systems. In each case the data have been fit to a Bleany–Bowers susceptibility expression

$$\chi_m = \frac{2g^2\beta^2N}{3k(T-\theta)}(1 + 1/3 \exp(-2J/kT))^{-1} + N\alpha$$

The parameter θ is the Curie–Weiss constant which can be shown to be a gauge of intermolecular interactions, and $N\alpha$ is the temperature independent paramagnetism (set equal to -120×10^{-6} cgs per dimer molecule). Fitting was accomplished as described in the Experimental Section. In general it can be said that a least-squares analysis of magnetic susceptibility data for antiferromagnetically coupled systems will give accurate exchange integral values, J ; however, the g values obtained will have an accuracy appreciably lower than obtainable with esr. For antiferromagnetic systems, the errors in J and g are not highly correlated. We have *not* elected to use the *apparent* g values from esr spectra for the three compounds in the least-squares fitting of the susceptibility data because computer simulation of the esr is required to determine the *actual* g values.

The molar paramagnetism, χ_m (corrected for the diamagnetism of the complex and for the background), of $[\text{Cu}_2(\text{tet-b})_2\text{Cl}](\text{ClO}_4)_3$ is plotted in Figure 6 as a function of temperature; the effective magnetic moment (μ_{eff}) vs. temperature curve is also given (see Table II for numerical values). An antiferromagnetic exchange interaction is present in this chloride-bridged copper(II) dimer, as evidenced (see Figure 6) by the $\mu_{\text{eff}} = 1.53$ BM at 290°K which drops smoothly to 0.15 BM at $\sim 30^\circ\text{K}$ and then remains level at ~ 0.15 BM down to 4.2°K. Least-squares fitting to the theoretical expression above gives $J = -144 \text{ cm}^{-1}$, $g = 2.31$, and $\theta = 1.0^\circ\text{K}$. The form of the exchange Hamiltonian used in this work results in the separation between the singlet ($S' = S_1 + S_2 = 0$) and triplet states of the dimer being equal to $2J$. The solid theoretical lines in Figure 6 are seen to fit the experimental points except in the very low-temperature region where the increase in χ_m is most probably due to the presence of a very small amount of some monomeric copper impurity.

The compound $[\text{Cu}_2(\text{tet-b})_2\text{Cl}](\text{ClO}_4)_3$ is the only reported monochloride-bridge copper(II) dimer and as such it is not possible to compare the observed exchange interaction with other Cu–Cl–Cu systems. However, a similar linear configuration involving a bromide bridge has been observed²⁶ in the polymeric compound CsCuBr_3 . A comparison of the magnetic and structural properties of this material and the structurally related compound CsCuCl_3 suggested that the room temperature diamagnetism of CsCuBr_3 is primarily due to a strong exchange interaction through the linear Cu–Br–Cu bridges between $[\text{Cu}_2\text{Br}_9]^{5-}$ dimers.

Di- μ -chloride bridging has been established for various copper(II) compounds. Very recently, Villa²⁷ reported an exchange interaction ($J = -50 \text{ cm}^{-1}$) propagated by a dichloride bridge in the dimer of tri-

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Table II. Experimental and Calculated Magnetic Susceptibility Results for $[\text{Cu}_2(\text{tet-b})_2\text{Cl}](\text{ClO}_4)_3$, $[\text{Cu}_2([14]4,11\text{-diene-N}_4)_2\text{CN}](\text{ClO}_4)_3$, and $[\text{Cu}_2(\text{tren})_2(\text{CN})_2](\text{BPh}_4)_2^c$

$[\text{Cu}_2(\text{tet-b})_2\text{Cl}](\text{ClO}_4)_3^b$					$[\text{Cu}_2([14]4,11\text{-diene-N}_4)_2\text{CN}](\text{ClO}_4)_3^b$				$[\text{Cu}_2(\text{tren})_2(\text{CN})_2](\text{BPh}_4)_2^c$					
$J = -144 \text{ cm}^{-1}$					$J = -4.87 \text{ cm}^{-1}$				$J = -1.82 \text{ cm}^{-1}$					
$g = 2.31$					$g = 2.18$				$g = 2.25$					
$\theta = 1.0^\circ\text{K}$					$\theta = 3.01^\circ\text{K}$				$\theta = -0.88^\circ\text{K}$					
$SE = 0.039^d$					$SE = 0.027^d$				$SE = 0.021^d$					
$T, ^\circ\text{K}$	$10^3\chi_m, \text{cgs}$		$\mu_{\text{eff}}/\text{Cu}, \text{BM}$		$10^3\chi_m, \text{cgs}$	Obsd	Calcd	$\mu_{\text{eff}}/\text{Cu}, \text{BM}$	Calcd	$T, ^\circ\text{K}$	$10^3\chi_m, \text{cgs}$		$\mu_{\text{eff}}/\text{Cu}, \text{BM}$	
	Obsd	Calcd	Obsd	Calcd							Obsd	Calcd	Obsd	Calcd
290	2.02	2.06	1.531	1.545	3.27	3.20	1.947	1.925		283	3.56	3.46	2.008	1.979
285	2.03	2.06	1.521	1.534						247.7	4.02	3.93	1.996	1.974
280	2.05	2.07	1.515	1.522						218.3	4.46	4.44	1.973	1.969
273	2.07	2.07	1.505	1.505						188.4	5.09	5.12	1.958	1.963
265	2.09	2.08	1.489	1.484						156.7	6.10	6.11	1.955	1.957
260	2.11	2.08	1.481	1.470						117.2	7.82	8.09	1.914	1.947
255	2.12	2.08	1.470	1.456	3.72	3.62	1.948	1.920		73.6	12.30	12.66	1.902	1.930
250	2.12	2.08	1.455	1.441						59.5	15.20	15.51	1.902	1.921
245	2.11	2.08	1.436	1.426						47.8	18.86	19.09	1.899	1.910
238	2.07	2.07	1.404	1.404						31.5	29.65	28.16	1.932	1.883
221	2.01	2.04	1.331	1.343	4.27	4.15	1.942	1.916		20.5	41.38	41.50	1.842	1.845
191	1.91	1.92	1.207	1.2121	4.80	4.78	1.915	1.912		15.7	52.41	52.29	1.814	1.812
160	1.69	1.67	1.040	1.035	5.62	5.68	1.895	1.907		11.7	65.67	66.68	1.753	1.766
121	1.19	1.12	0.757	0.736	7.23	7.47	1.870	1.901		9.3	79.73	79.71	1.722	1.722
80	0.39	0.41	0.354	0.360	10.91	11.19	1.868	1.892		7.3	95.48	94.94	1.669	1.665
64.5	0.17	0.22	0.208	0.240	13.63	13.92	1.868	1.888		5.6	113.4	112.6	1.594	1.589
51.0	0.11	0.14	0.150	0.171	16.69	17.37	1.845	1.882		4.7	123.5	124.4	1.524	1.529
33.5	0.16	0.12	0.146	0.127	24.45	26.05	1.810	1.868		4.2	131.6	131.6	1.487	1.486
29.2					30.60	29.68	1.890	1.862						
24.7					35.19	34.70	1.864	1.851						
20.5					42.12	41.13	1.858	1.836						
17.0					50.66	48.49	1.856	1.815						
13.0	0.45	0.12	0.154	0.079	59.81	60.33	1.763	1.771						
11.6					67.86	65.64	1.774	1.745						
9.6					74.57	74.31	1.692	1.689						
8.0	0.78	0.12	0.158	0.062	80.30	81.76	1.603	1.617						
6.7					85.46	87.28	1.513	1.529						
5.6					90.40	90.68	1.423	1.425						
4.2	1.20	0.12	0.142	0.045	96.35	96.38	1.272	1.272						

^a Diamagnetic corrections used: -556.9×10^{-6} for the chloride, -500.5×10^{-6} for the monocyanoide, and -675.7×10^{-6} for the dicyanoide. ^b Data taken at a magnetic field of 54.3 kG. ^c Data taken at a magnetic field of 14.8 kG. ^d $SE = \{ \sum_{i=1}^n |\mu_{\text{eff}}(\text{obsd})_i - \mu_{\text{eff}}(\text{calcd})_i|^2 / (n - K) \}^{1/2}$, where n = number of observables and K = number of parameters.

chloroguaniumcopper(II) monohydrate. The X-ray crystal structure of this dimer has been reported²⁸ and the copper environment is found to be a slightly distorted trigonal bipyramid. The dichloride bridging in this system is effected by a chloride in both the equatorial and the axial positions, yet the exchange interaction is weaker than that for $[\text{Cu}_2(\text{tet-b})_2\text{Cl}](\text{ClO}_4)_3$. This can be taken as additional evidence for the importance of a linear Cu-Cl-Cu bridge in the propagation of exchange interaction, even when the bridge is equatorial. The reduced antiferromagnetic coupling in the angular Cu-Cl-Cu bridge is most likely due to ferromagnetic pathways partially offsetting the antiferromagnetic contributions. There are other dichloride-bridged copper systems known, but they possess other than trigonal bipyramidal geometry, precluding a simple comparison of exchange interactions.

Variable-temperature magnetic susceptibility data are reported in Table II for $[\text{Cu}_2([14]4,11\text{-diene-N}_4)_2\text{CN}](\text{ClO}_4)_3$. At 283°K μ_{eff} (per copper) is 1.95 BM and remains relatively constant to ~20°K whereupon there is an attenuation due to an antiferromagnetic interaction. The μ_{eff} value at 4.2°K is 1.27 BM (per copper), which is appreciably lower than the spin-only value. Least-squares fitting gives $J = -4.8 \text{ cm}^{-1}$,

$g = 2.18$, and $\theta = 3.01^\circ\text{K}$. In comparison to the chloride-bridged dimer, there has been a considerable reduction in the exchange interaction in going to the Cu-CN-Cu bridge. The change in exchange interaction could be due to two factors. The character of the bridge and the extent of interaction with the copper atoms is one important factor. Certainly the more extended nature of the cyanide bridge compared with the chloride bridge as well as the likelihood that the Cu-NC interaction is relatively weak lead to an attenuation in the interaction in going from Cu-Cl-Cu to Cu-CN-Cu. An extension of this consideration is that for the Cu-Cl-Cu system the copper orbitals are forced by symmetry to bond into the *same* chlorine orbital, whereas for Cu-CN-Cu this restriction is not present; thus the interaction may be reduced due to this reduced overlap. The second probable factor leading to the attenuation is the change in orientation of the g tensors at the copper centers relative to the bridge position. This tilting of the g axes from the bridge direction could be caused by either different Cu-bridge bond strengths or by a difference in distortion of the trigonal bipyramidal coordination due to the steric requirements of the backside ligands. (The geometry of the CN system is seen to be more distorted than is that of the Cl system.) The observed variation of the J values is undoubtedly due to a combination of the two above factors.

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A comparison of the magnetism of the two cyanide-bridged dimers, to which we now turn, is enlightening. As described in the Molecular Structures section, the compound $[\text{Cu}_2(\text{tren})_2(\text{CN})_2](\text{BPh}_4)_2$ is bridged by cyanide groups hydrogen bonding to tren nitrogens. *A priori*, the possibility of having an exchange interaction large enough to see with susceptibility measurements to 4.2°K would have been discounted. However, as Table II indicates, the compound has at 283°K a μ_{eff} per copper of 2.00 BM which is relatively constant to 50°K where it then decreases to 1.52 BM at 4.2°K. An appreciable antiferromagnetic interaction is present. Least-squares fitting of the data gives $J = -1.8 \text{ cm}^{-1}$, $g = 2.25$, and $\theta = -0.88^\circ\text{K}$. While this is not an exceptionally large exchange integral, it is clear that there is an interaction which is easily measurable and the bridging unit which gives rise to this coupling includes a hydrogen bond. The presence of the large BPh_4^- counterion and the packing details of BPh_4^- and $[\text{Cu}_2(\text{tren})_2(\text{CN})_2]^{2+}$ eliminate the possibility of an appreciable intermolecular interaction.

The presence of an exchange interaction propagated between copper(II) centers by a hydrogen-bonded cyanide group could be relevant to many observations on cuproproteins. Cyanide ion has been found to bind to the copper site in some cuproproteins (e.g., superoxide dismutase),²⁹ resulting in dramatic changes in the physical properties of the protein. Even further, many other small ions, with potential for hydrogen bonding, notably N_3^- and F^- , have been detected to alter the properties of various cuproproteins,³⁰ many of which are believed to have two or more copper atoms per molecule.

It is interesting to note that although the mono-cyanide-bridged complex has a much more direct bridge than does $[\text{Cu}_2(\text{tren})_2(\text{CN})_2](\text{BPh}_4)_2$, its net exchange interaction is *not* as much larger as would be expected on this basis. The explanation for this must again be found in the orientation of the bridging assembly with respect to the copper unpaired electron density (i.e., g tensor). In the tren system the cyanide ligand is in an axial position as opposed to the equatorial cyanide in $[\text{Cu}_2([14]4,11\text{-diene-N}_4)_2\text{CN}](\text{ClO}_4)_3$. Since the unpaired electron in both of these distorted trigonal bipyramidal systems is in an orbital of predominantly d_{z^2} character (i.e., axial), the cyanide of the tren dimer would be more effective in transferring unpaired spin density, effective enough even to provide sufficient density to transfer through the hydrogen bond to the second copper *via* an equatorial tren nitrogen. In respect to some of our previous discussions concerning σ and π pathways in exchange mechanisms,³¹ the exchange interaction through the hydrogen bond is seemingly the first clear cut example of a σ only pathway.

Conclusion

Two different types of cyanide bridging, Cu-CN-Cu and Cu-CN···HN-Cu, have been found with crystal structural work on two copper(II) dimers. The

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intensity of the CN ir band has been suggested as a criterion of such end-to-end cyanide bridging. The orientation with respect to the bridging group of the copper orbital containing the unpaired electron has been shown to be important for determining the J values, and an interaction through a purely σ -bonded system has been detected.

Experimental Section

Compound Preparation. The compound $[\text{Cu}_2([14]4,11\text{-diene-N}_4)_2\text{CN}](\text{ClO}_4)_3$ was prepared by the method of Curtis.⁵ Mixing equimolar amounts of $\text{Cu}([14]4,11\text{-diene-N}_4)(\text{ClO}_4)_2$ and NaCN in methanol immediately gives a blue precipitate of the dimer. Alternatively, the same reactants may be combined in a small quantity of dimethyl sulfoxide (DMSO) and an excess of isopropyl alcohol added, causing a microcrystalline product to form over a period of a few days. Larger crystals are obtained by slow diffusion of isopropyl alcohol into a DMSO solution of the reactants. Satisfactory elemental analyses were obtained in all cases without further purification.

The preparation of $[\text{Cu}_2(\text{tren})_2(\text{CN})_2](\text{BPh}_4)_2$ was carried out with a procedure identical with that reported^{22,30} for the preparation of other $[\text{Me}_2(\text{tren})_2\text{X}_2]^{2+}$ species, with the exception that the polyamine ligands used to prepare $[\text{Cu}_2(\text{tren})_2(\text{CN})_2](\text{BPh}_4)_2$ are ostensibly tren, triethylenetetramine. As commercial tren (Aldrich) is 10–20% tren and we add in general only a small amount (~10–20% of the molar equivalent) of NaBPh₄ to our aqueous solutions as a precipitating agent, it is clear that the tren complex forms much more readily than the trien analog. The determination of the identity of the ligand coordinated was possible through scrutiny of the ir spectrum of the material in the 1100–1400-cm⁻¹ region and was proven by X-ray structural analysis. Single crystals were obtained by slow evaporation of an acetonitrile solution of the complex. Two crystal habits were observed, one of monoclinic dimensions and the other consisting of six-sided plates. The precession photographs for both forms were identical in all respects. Data were collected on the six-sided crystals. It should also be noted that $[\text{Cu}_2(\text{tren})_2(\text{CN})_2](\text{BPh}_4)_2$ may also be prepared in the more conventional manner, using tren (Ames Laboratories).

The compound $[\text{Cu}_2(\text{tet-b})_2\text{Cl}](\text{ClO}_4)_3$ was synthesized for magnetic studies following the procedure of Bauer, *et al.*¹⁶ The free tet-b³² ligand initially reacts with $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in an aqueous solution made basic with 1 *M* NaOH to form a blue complex. Acidifying after ~10 sec with 1 *M* HClO₄ to a pH <3 prevents formation of an intermediate red species. Subsequent addition of 2 g of NaClO₄ and a five-fold excess of NaCl to the solution causes precipitation of the chloride bridged compound. The product was recrystallized three times from 0.01 *M* HClO₄ prior to use.

It has already been noted¹⁶ that the analogous bromide and iodide complexes could not be prepared, and we have attempted to synthesize the analog of the chloride bridged species with the [14]4,11-diene-N₄ ligand in methanol and propylene carbonate by adding THF or isopropyl alcohol to precipitate the complex. Only monomeric products were obtained in these attempts.

Physical Measurements. Infrared spectra were run with a Perkin-Elmer Model 457 spectrophotometer using 13-mm KBr pellets or Nujol mulls between KBr plates. Electronic absorption data were measured using a Cary 14 spectrophotometer. Here, again, both KBr pellets and Nujol mulls were used. For the dicyanide system pellet dispersion was compensated by employing a pellet of ~1% NaBPh₄ in KBr in the reference beam. Q-Band esr spectra were recorded using a Varian E-110 microwave bridge in conjunction with a 12-in. 25 kG magnet. Variable-temperature (4.2–283°K) magnetic susceptibility measurements were made using a Princeton Applied Research Model 150A magnetometer as described in a previous paper.³³

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