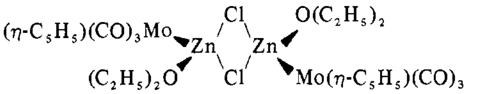
and are displaced so as to allow the Zn to occupy a position trans to one carbonyl group.

Comparison of η-$C_5H_5(CO)_3MoZnBr\cdot 2THF$ with its chloride analogue grown from ether solution shows the difference in coordination ability of diethyl ether and tetrahydrofuran. When the chloride derivative is precipitated from diethyl ether, a dimer forms[1] with bridging chloride ions as indicated in I. The ether molecule occupying the fourth coordination position of the zinc is easily lost giving rise to the anomalous low-energy infrared band which has been ascribed[1] to $Zn\leftarrow O—C$ interactions. The present compound which contains bromide ions and THF molecules forms a monomer with two coordination sites on zinc occupied by THF oxygen atoms. The first THF can be removed readily, presumably yielding a molecule analogous to that observed for the chloride with a bridging bromide and a coordinated THF molecule. Removal of the second THF molecule does not occur readily.



Therefore, it appears that the change between the chloride and bromide from dimer to monomer is associated with the increased ability of the THF to coordinate the zinc atom over that of diethyl ether. Thus, the loss of ether gives rise to the formation of the stable dimeric structure observed.

Registry No. $[(n\text{-}C_6H_9)_4N][\eta\text{-}C_5H_5(CO)_3Mo]$, 61618-13-1; η-$C_5H_5(CO)_3MoZnBr\cdot 2THF$, 61618-14-2.

Supplementary Material Available: Listings of observed and calculated structure amplitudes and stereoscopic views of molecular packing (16 pages). Ordering information is given on any current masthead page.

References and Notes

(1) J. St. Denis, W. Butler, M. D. Glick, and J. P. Oliver, *J. Am. Chem. Soc.*, **96**, 5427 (1974).
(2) D. E. Crotty and J. P. Oliver, submitted for publication.
(3) (a) Local versions of the following programs were used: SYNCOR, W. Schmonsees' program for data reduction; NEWES, W. Schmonsees' program for generation of normalized structure factors; REL, R. E. Long's program for phase determination by Sayre's method; FORDAP, A. Zalkin's Fourier program; ORFLS and ORFFE, W. Busing, K. Martin, and H. Levy's full-matrix least-squares program and function and error program; ORTEP, C. K. Johnson's program for drawing crystal models; HFINDER, A. Zalkin's idealized hydrogen program, modified by T. J. Anderson. (b) Scattering factors for Mo, Zn, Br, O, N, C, and H, including anomalous scattering for Mo, Zn, and Br, were taken from "International Tables for X-Ray Crystallography", Vol. IV, J. A. Ibers and W. C. Hamilton, Ed., Kynoch Press, Birmingham, England, 1974.
(4) A. F. Berndt and R. E. Marsh, *Acta Crystallogr.*, **16**, 118 (1963).
(5) F. C. Wilson and D. P. Shoemaker, *J. Chem. Phys.*, **27**, 809 (1957).
(6) M. J. Bennett and R. Mason, *Proc. Chem. Soc., London*, 273 (1963).
(7) S. Chaiwasie and R. H. Fehn, *Acta Crystallogr., Sect. B*, **24**, 525 (1968).
(8) J. Rajaram and J. A. Ibers, *Inorg. Chem.*, **12**, 1313 (1973).
(9) Supplementary material.

Contribution from the School of Chemical Sciences,
University of Illinois, Urbana, Illinois 61801

Magnetic Exchange in Transition Metal Dimers. 9. Copper(II) Dimers with Single End-to-End Cyanide Bridges and Unusual Electron Paramagnetic Resonance Spectra

DAVID S. BIEKSZA and DAVID N. HENDRICKSON*[1]

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The preparation of three Cu(II) dimers, $[Cu_2(bpy)_4(CN)](PF_6)_3$ where bpy is 2,2′-bipyridine, $[Cu_2(phen)_4(CN)](PF_6)_3$ where phen is 1,10-phenanthroline, and $[Cu_2(tren)_2(CN)](PF_6)_3$ where tren is 2,2′,2″-triaminotriethylamine, is reported. A single cyanide ion bridges in an end-to-end fashion in each of these compounds. An antiferromagnetic exchange interaction is present in each dimer, as evidenced by variable-temperature (4.2–267 K) magnetic susceptibility data. Exchange parameters (J) are found to be −9.4, −29, and −88 cm^{-1}, respectively, by least-squares fitting to the spin Hamiltonian, $\hat{H} = -2J\hat{S}_1\cdot\hat{S}_2$. Essentially isotropic signals at $g \simeq 2.1$ are seen in the X-band and Q-band EPR spectra of all three compounds with the exception of the Q-band spectrum of the bipyridine compound where signals at $g = 2.165$ and 2.118 are seen. The local Cu(II) ion environments are most probably trigonal bipyramidal in these three dissimilar ion dimers and the isotropic signals are shown to result from an *intradimer* electron exchange that averages the **g** tensors of the two different Cu(II) ions.

Introduction

Cyanide ions are known to bridge in an end-to-end fashion between transition metal ions in polymeric and dimeric complexes.[2–6] As recent as 1971, the first x-ray structure of a dimeric complex with a single end-to-end cyanide bridge was reported[7] for $(NC)_5Co\text{-}CN\text{-}Co(NH_3)_5\cdot H_2O$. A few years later, the x-ray structure and the presence of an antiferromagnetic exchange interaction were reported for $[Cu_2([14]4,11\text{-diene-}N_4)_2(CN)](ClO_4)_3$, where [14]4,11-diene-$N_4$ is 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene.[8] The local copper atom environments in the dimeric cation were found to be distorted trigonal bipyramids. The $J = -4.8$ cm^{-1} exchange interaction is effected by the cyanide ion bridging from an equatorial site on one Cu(II) ion to an equatorial site on the second Cu(II) ion.

In this paper, we report the preparation of three new dimeric Cu(II) complexes that also are bridged by a single cyanide ion in an end-to-end fashion. The three complexes were prepared, on the one hand, to further investigate magnetic exchange interactions between Cu(II) ions as propagated by cyanide ions. It was of interest to see how large the antiferromagnetic interaction could become with this bridge. More importantly, we were interested in such Cu–CN–Cu complexes because they are examples of rarely encountered paramagnetic dimers in which the two metal ions are in slightly different environments. In a cyanide-bridged copper dimer, obviously, one Cu(II) ion is bonded to the nitrogen atom and the other to the carbon atom of the cyanide ion. In such dissimilar-ion dimers, an increase in the exchange interaction from a negligible J value (relative to the difference in g values) to an appreciable J value results in dramatic changes in the EPR spectra of the complexes as a consequence of the increasing frequency at which electrons exchange between the two Cu(II) ions.

Experimental Section

Compound Preparation. Samples of $[Cu_2(phen)_4(CN)](PF_6)_3$ were prepared in the following way. In 200 mL of distilled water were dissolved 0.24 g of $Cu(NO_3)_2\cdot 3H_2O$ and 0.40 g of 1,10-phenanthroline. Dilute nitric acid was added to adjust the pH of the solution to 1.75. An aqueous solution of 0.15 g of NaCN (sixfold stoichiometric excess) was added (*in hood*), followed by an aqueous solution of 0.24 g of NH_4PF_6. A blue-green powder precipitated almost immediately. Recrystallization by slow evaporation of an acetonitrile solution gave crystals in the form of very dark green rectangular plates. Anal. Calcd for $[Cu_2C_{49}H_{32}N_9](PF_6)_3$: Cu, 9.71; C, 44.96; H, 2.47; N, 9.63. Found: Cu, 9.70; C, 45.01; H, 2.52; N, 9.67.

Samples of **$[Cu_2(bpy)_4(CN)](PF_6)_3$** were prepared by dissolving 0.24 g of $Cu(NO_3)_2{\cdot}3H_2O$ and 0.31 g of 2,2′-bipyridine in 200 mL of distilled water, followed by adjusting the solution pH to 2.00 with dilute nitric acid. Addition of an aqueous solution (*in hood*) of 0.10 g of NaCN (fourfold stoichiometric excess) resulted in the precipitation of a small amount of purple powder, which was filtered. To the filtrate was added an aqueous solution of 0.24 g of NH_4PF_6. A blue powder formed over a period of several hours. Anal. Calcd for $[Cu_2C_{41}H_{32}N_9](PF_6)_3$: Cu, 10.48; C, 40.60; H, 2.67; N, 10.40. Found: Cu, 10.56; C, 40.76; H, 2.89; N, 10.57.

Samples of **$[Cu_2(tren)_2(CN)](PF_6)_3$** were prepared by successively dissolving 0.50 g of $CuSO_4{\cdot}5H_2O$, 0.3 mL of 2,2′,2″-triaminotriethylamine (tren), 0.05 g of NaCN, and 0.24 g of NH_4PF_6 in 50 mL of distilled water. After evaporation of the solution to a volume of 10 mL, dark blue crystals were obtained. Anal. Calcd for $[Cu_2C_{13}H_{36}N_9](PF_6)_3$: Cu, 14.43; C, 17.73; H, 4.13; N, 14.32. Found: Cu, 14.61; C, 17.71; H, 3.89; N, 14.34.

Analytical data were obtained in the School of Chemical Sciences microanalytical laboratory.

Physical Measurements. Infrared spectra were obtained on a PE Model 467 spectrophotometer; each sample was prepared as a KBr pellet. The EPR instrumentation (both X and Q band) and procedure for variable-temperature magnetic susceptibility determination have been previously described.[9] The magnetic susceptibility data were least-squares fit with an adapted version of the computer function minimization program known as STEPT.[10]

Results and Discussion

Compound Preparation. In the preparations of $[Cu_2(phen)_4(CN)](PF_6)_3$ and $[Cu_2(bpy)_4(CN)](PF_6)_3$, we have found that adjusting the pH of the solution before adding a solution of NH_4PF_6 proved to be a critical factor. In the case of the phenanthroline compound, a purple precipitate forms upon addition of a NaCN solution to a solution of Cu(II) ion and phenanthroline, *if the pH of the solution is above 2.0.* This purple precipitate analyzes to be $Cu(phen)(CN)_2$. Below a pH of 1.5, the only product that precipitates upon adding the PF_6^- was found to analyze as $[Cu(phen)_2(NO_3)]PF_6$. Thus, it is necessary to adjust the pH of the solution to ~1.75 to get $[Cu(phen)_4(CN)](PF_6)_3$.

In the case of the bipyridine compound, adjusting the pH to less than 1.9 for a solution of $Cu(NO_3)_2{\cdot}3H_2O$, NaCN, and NH_4PF_6 gave $[Cu(bpy)_2(NO_3)]PF_6$. Some small amount of a purple solid, as in the phenanthroline case, was obtained at all pH values. A pH of 2.00 was found to be best to obtain $[Cu_2(bpy)_4(CN)](PF_6)_3$.

No solution pH adjustment was necessary in the preparation of the tren compound. It is known that tren with its tripodal construction enforces a five-coordinate, trigonal-bipyramidal geometry on a Cu(II) ion.[11] Thus, the cyanide ion occupies the last coordination site which is axial in the aqueous species $[Cu(tren)(CN)]^+$. If this aqueous species is precipitated with a water solution of $NaBPh_4$, the compound obtained is $[Cu_2(tren)_2(CN)_2](BPh_4)_2$, the structure of which has been reported[12] to consist of discrete cations of hydrogen-bonded pairs of $[Cu(tren)(CN)]^+$ ions and discrete BPh_4^- ions. We have found that using PF_6^- in place of BPh_4^- gives, upon evaporation of the solution, a dark blue compound that analyzes to be $[Cu_2(tren)_2(CN)](PF_6)_3$.

Infrared Spectra. The KBr-pellet IR spectra of $[Cu_2(phen)_4(CN)](PF_6)_3$, $[Cu_2(bpy)_4(CN)](PF_6)_3$, and $[Cu_2(tren)_4(CN)](PF_6)_3$ are reproduced in Figure 1. The most important feature in each of these spectra is the cyanide stretching band which is seen at 2160, 2140, and 2150 cm^{-1}, respectively. It is also important to note that, in each case, the cyanide stretching band is quite weak. The work of Dows et al.[13] indicated that, with the assumption of similar bond strengths for both terminally bound and bridging cyanide ions, the cyanide stretching frequency should be significantly greater for the bridging case compared to the terminal cyanide case. The three compounds prepared in this work have cyanide stretching frequencies which are in the range characteristic of end-to-end bridging cyanide ions. Furthermore, the low intensity of the cyanide bands (see Figure 1) also can indicate an end-to-end bridging of the cyanide ion. Such a low-intensity cyanide band was seen for $[Cu_2[14]4,11\text{-diene-}N_4)_2(CN)](ClO_4)_3$, which has been shown with an x-ray structure[8] to have an end-to-end bridging cyanide ion.

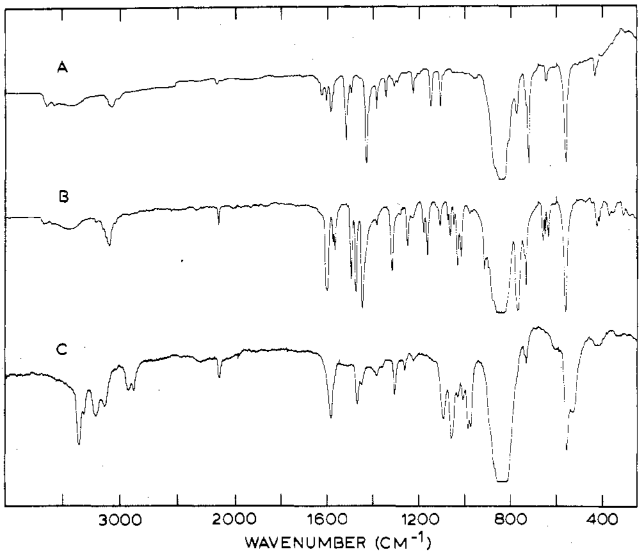


Figure 1. Infrared spectra (KBr pellets) of $[Cu_2(phen)_4(CN)](PF_6)_3$ (A), $[Cu_2(bpy)_4(CN)](PF_6)_3$ (B), and $[Cu_2(tren)_2(CN)](PF_6)_3$ (C).

The high frequency and low intensity of the cyanide bands of our three compounds do not necessarily mean that the cyanide ions in the compounds are end-to-end bridging between the two copper ions. The cyanide IR band of $[Cu_2(tren)_2(CN)_2](BPh_4)_2$ is found at 2140 cm^{-1} and also is of low intensity.[8] In this compound, the nitrogen atom of each cyanide ion is *not* bonded to a Cu(II) ion but is hydrogen bonded to a tren nitrogen atom. The compound $[Cu(phen)_2(CN)]NO_3{\cdot}H_2O$ also has a low-intensity, high-frequency cyanide stretching band. A recent x-ray structure[14] shows that this results from the coordinated cyanide ion hydrogen bonding via its nitrogen atom with the water molecule. In view of these facts, it was necessary to turn to other physical techniques to show that we do have end-to-end cyanide-bridged Cu(II) dimers in our three compounds.

Magnetic Susceptibility and Exchange Mechanism. As depicted in Figures 2–4 (the data are given in the supplementary material), the compounds $[Cu_2(bpy)_4(CN)](PF_6)_3$, $[Cu_2(phen)_4(CN)](PF_6)_3$, and $[Cu_2(tren)_2(CN)](PF_6)_3$ have magnetic susceptibility curves that are characteristic of an antiferromagnetic exchange interaction. In the case of the first compound, there is a maximum (Néel temperature) in the magnetic susceptibility at 18 K and the effective magnetic moment per Cu(II) ion varies from 1.88 μ_B at 267 K to 0.56 μ_B at 4.2 K (see Figure 2). The data for this bipyridine compound were least-squares fit to the Bleaney–Bowers equation[15] for an isotropic exchange interaction in a Cu(II) dimer, $\hat{H} = -2J\hat{S}_1{\cdot}\hat{S}_2$ where J is the exchange parameter and $\hat{S}_1$ and $\hat{S}_2$ are the spin operators for the two Cu(II) ions. The average g value was taken as 2.103 (from the EPR; vide infra) and kept constant as the exchange parameter was varied to fit the data. The least-squares fit obtained in this manner gives $J = -9.4$ cm^{-1} and is represented in Figure 2 as solid lines. As can be seen, the μ_{eff}/Cu data are fit reasonably well down

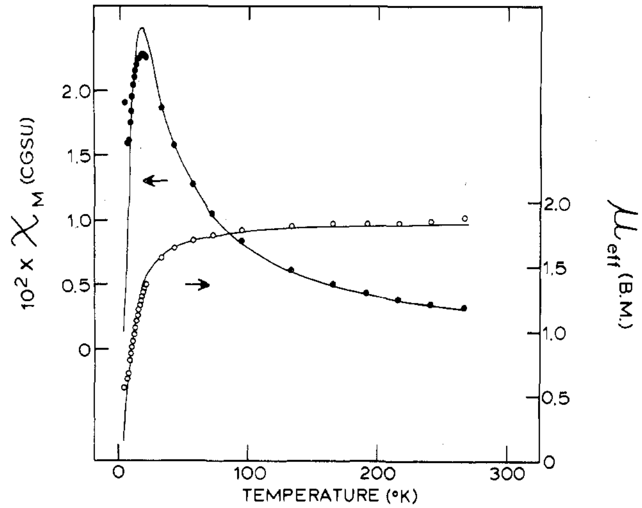


Figure 2. Molar paramagnetic susceptibility (χ_M per dimer, cgsu/mol) and effective magnetic moment per copper ion (μ_{eff}) of $[Cu_2(bpy)_4(CN)](PF_6)_3$ plotted as a function of temperature. The solid lines result from least-squares fitting to the theoretical model.

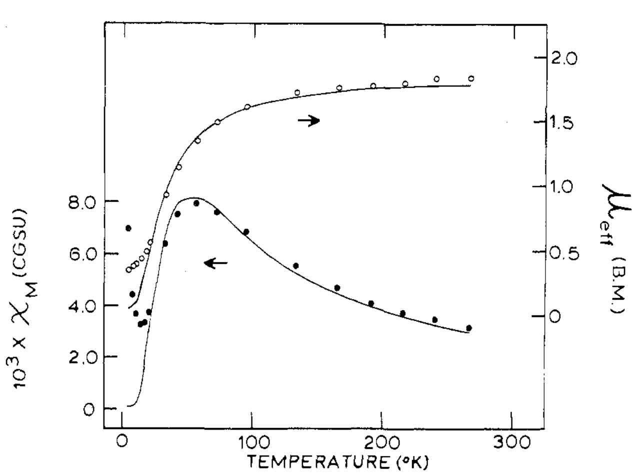


Figure 3. Molar paramagnetic susceptibility (χ_M per dimer, cgsu/mol) and effective magnetic moment per copper ion (μ_{eff}) of $[Cu_2(phen)_4(CN)](PF_6)_3$ plotted as a function of temperature. The solid lines result from least-squares fitting to the theoretical model.

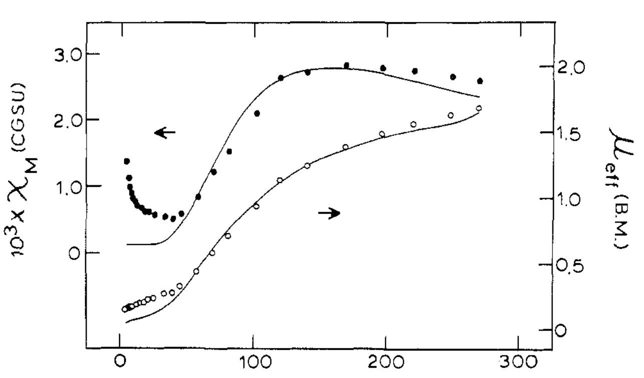


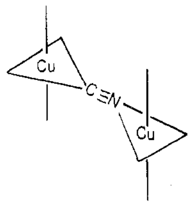
Figure 4. Molar paramagnetic susceptibility (χ_M per dimer, cgsu/mol) and effective magnetic moment per copper ion (μ_{eff}) of $[Cu_2(tren)_2(CN)](PF_6)_3$ plotted as a function of temperature. The solid lines result from least-squares fitting to the theoretical model.

to ~10 K, below which the experimental value approaches ~0.5 μ_B, whereas the calculated value goes below ~0.2 μ_B. Such a deviation is quite frequently seen for Cu(II) dimers with relatively weak antiferromagnetic exchange interactions and is attributed to the presence of monomeric Cu(II) impurities.[16] In Figure 2, it can also be seen that the theoretical fit of χ_M deviates from the experimental data. The deviation in fitting the χ_M curve appears to be greater than for the μ_{eff}/Cu curve, because χ_M is a more rapidly changing function of temperature than μ_{eff}/Cu. It is clear that the addition of another parameter to account for the monomer impurity, which is probably less than ~3% by weight, would improve the fit.

The magnetic susceptibility data (Figure 3) for $[Cu_2(phen)_4(CN)](PF_6)_3$ were least-squares fit to the same equation, this time holding $\bar{g}$ = 2.114 (from the EPR), and this gave $J = -29$ cm^{-1}. The larger (negative) exchange parameter is a reflection of the fact that in this case the susceptibility peaks at ~57 K and the μ_{eff}/Cu value drops below a spin-only value at a higher temperature than in the bipyridine case. The χ_M data for the phenanthroline compound are better fit in the maximum (~57 K) region, because the antiferromagnetic interaction is appreciably larger and the effects of small amounts of impurities show up at the lowest temperatures.

By far, the greatest antiferromagnetic exchange interaction is present in $[Cu_2(tren)_2(CN)](PF_6)_3$, as can be seen in Figure 4. In this case, the maximum in χ_M occurs at ~170 K and the μ_{eff}/Cu value is already below a spin-only value at 267 K. With $\bar{g}$ = 2.117 (from EPR), least-squares fitting gives $J = -88$ cm^{-1}. The μ_{eff}/Cu value at 4.2 K is only 0.16 μ_B and, as such, it can be concluded that there is very little monomeric Cu(II) impurity. In fitting all three compounds, a TIP of 120 $\times 10^{-6}$ cgsu/mol of dimer has been used.

From the IR and magnetic susceptibility measurements (and analytical data), it can be concluded that each of our three compounds does have dimeric Cu(II) cations that are bridged in an end-to-end fashion by cyanide ions. On the basis of previous x-ray structural work on Cu(II) complexes with phenanthroline, bipyridine, and 2,2′,2″-triaminotriethylamine, it is possible to deduce the basic structural features of our three Cu(II) dimers. Phenanthroline and bipyridine are similar in their metal coordination tendencies and it is known that neither is capable of square-planar coordination at Cu(II) for steric reasons.[17] X-ray work on such Cu(II) complexes has shown that $(phen)_2$ and $(bpy)_2$ complexes of Cu(II) are five-coordinate and are trigonal bipyramidal. Each of the bidentate phen (or bpy) ligands occupies one axial and one equatorial position. Thus, in a $[Cu(phen)_2X]^+$ or $[Cu(bpy)_2X]^+$ (X = anion) complex, the X^- group takes an equatorial coordination site. The $[Cu_2(phen)_4(CN)]^{3+}$ and $[Cu_2(bpy)_4(CN)]^{3+}$ species each consist of two trigonal-bipyramidal Cu(II) moieties bridged from one equatorial site to another by a cyanide ion in an end-to-end fashion. This is schematically illustrated as dimer I. The ligand tren also leads to a trigonal-bipyramidal Cu(II) coordination, as evidenced by various x-ray structures.[11,12] Because tren is tripodal in construction, the tertiary nitrogen atom of tren occupies one axial position with the three other tren nitrogen atoms taking the three equatorial positions. This leaves only the one axial position open. Thus, $[Cu_2(tren)_2(CN)]^{3+}$ consists of two trigonal-bipyramidal Cu(II) moieties bridged from one axial site to another. This is



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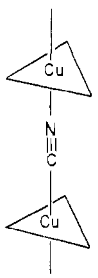

II

schematically indicated as dimer II.

With structures I and II, it is possible to understand the variation of exchange parameter in the series $[Cu_2(bpy)_4(CN)](PF_6)_3$ ($J = -9.4$ cm^{-1}), $[Cu_2(phen)_4(CN)](PF_6)_3$ ($J = -29$ cm^{-1}), and $[Cu_2(tren)_2(CN)](PF_6)_3$ ($J = -88$ cm^{-1}). In the ground state of a trigonal-bipyramidal Cu(II) complex, the single unpaired electron is located in an essentially d_{z^2} orbital. In the case of dimer II, the two trigonal bipyramids are oriented such that the main lobes of the d_{z^2} orbitals located at each Cu(II) center are pointed at the bridging cyanide ion. This results in the strongest antiferromagnetic exchange interaction. An ab initio MO calculation[18] for CN^- shows that the eight valence electrons are found in four molecular orbitals with the following symmetries (energies): 3σ (−4.40 eV), π (−4.75 eV), 2σ (−8.25 eV), 1σ (−24.73 eV). The symmetry of the Cu(II) d_{z^2} orbitals is such that they can overlap with the 1σ, 2σ, and 3σ cyanide orbitals in dimer II and this overlapping leads, in the net, to an antiferromagnetic exchange interaction. The compound $[Cu_2(tren)_2(CN)](PF_6)_3$ has a dimer II type cation and this explains the large negative J value of −88 cm^{-1}.

The weaker antiferromagnetic exchange interactions in the phenanthroline and bipyridine cations are explicable in terms of a structure approaching that of dimer I. The copper d_{z^2} orbitals are oriented in dimer I such that only the relatively less important "doughnuts" of the d_{z^2} orbitals overlap with the σ orbitals of the cyanide ion and this reduced overlap leads to a reduced antiferromagnetic interaction between the two Cu(II) unpaired electrons. The bipyridine dimer would be expected to approximate more closely than the phenanthroline dimer to the idealized geometry (i.e., trigonal-bipyramidal Cu(II) ions) of dimer I and this leads to a J value of −9.4 cm^{-1}. We are reminded that the structure of the cyanide-bridged cation in $[Cu_2([14]4,11\text{-diene-}N_4)_2(CN)](ClO_4)_3$ is somewhat distorted[8] from the idealized geometry of dimer I and in this case $J = -4.8$ cm^{-1}. Phenanthroline has a more restricted "bite" than bipyridine and this leads to a greater distortion from trigonal-bipyramidal Cu(II) ion environment than in the bipyridine dimer. The increased distortion could result in a change in the orientation of the z axis relative to the cyanide ion, which, in effect, partially brings the main lobe of the d_{z^2} orbital into overlap with the σ cyanide orbitals, or the increased distortion could mix in some amount of $d_{x^2-y^2}$ into the ground state. Either of these possibilities would lead to greater antiferromagnetic exchange interacton in $[Cu_2(phen)_4(CN)]^{3+}$ than in $[Cu_2(bpy)_4(CN)]^{3+}$. X-ray structural work is needed.

Electron Paramagnetic Resonance. The room-temperature Q-band EPR spectrum of $[Cu_2(phen)_4(CN)](PF_6)_3$ is illustrated in Figure 5, tracing A. As can be seen, the signal consists of a single somewhat asymmetric derivative at a g value of 2.126. For comparison, the Q-band spectra of $[Cu(phen)_2(CN)]NO_3{\cdot}H_2O$ (tracing B) and $[Cu(phen)_2(CN)]PF_6$ (tracing C) are also shown in Figure 5. Both of these compounds have monomeric Cu(II) cations and, as we mentioned above, the x-ray structure of the former has been reported.[14] The spectra of these two monomers are essentially identical and they are characteristic of the distorted trigonal-bipyramidal geometry of monomeric $Cu(phen)_2(CN)^+$. The trigonal-bipyramidal $d^1_{z^2}$ ground state is expected to have a $g_\parallel$ value close to 2.0. For $[Cu(phen)_2(CN)]NO_3{\cdot}H_2O$, we find g values of 2.242, 2.149, and 2.054.

In Figure 6 are illustrated the room-temperature Q-band spectra of $[Cu_2(bpy)_4(CN)](PF_6)_3$ (tracing A) and $[Cu_2(tren)_2(CN)](PF_6)_3$ (tracing B). As with the phenanthroline compound, the tren compound gives a single derivative, this time at a g value of 2.117. A single derivative is *not* what is seen for a *monomeric* $Cu(tren)X^+$ species, but such a monomer typically gives a $g_\parallel$ signal at 2.01 and a $g_\perp$ signal at 2.15.[9] The latter signal will be split if the $Cu(tren)X^+$ species is distorted from axial symmetry. As in the phenanthroline case, it must be emphasized that the single derivative that is seen for $[Cu_2(tren)_2(CN)](PF_6)_3$ does *not* correspond to a broadened, unresolved version of a monomer spectrum or a superposition of two broad monomer spectra.

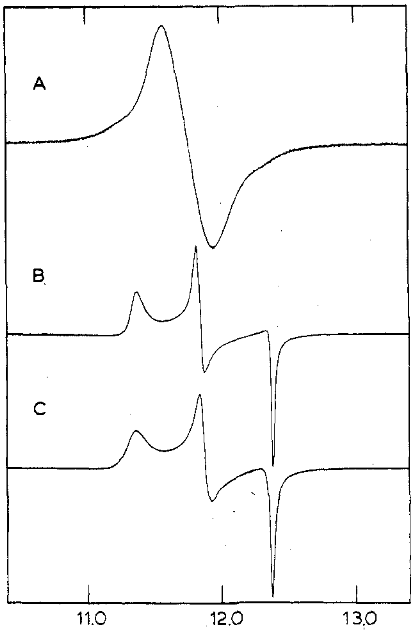

Figure 5. Room-temperature Q-band EPR spectra of powdered samples of $[Cu_2(phen)_4(CN)](PF_6)_3$ (A), $[Cu(phen)_2(CN)]NO_3{\cdot}H_2O$ (B), and $[Cu(phen)_2(CN)]PF_6$ (C).

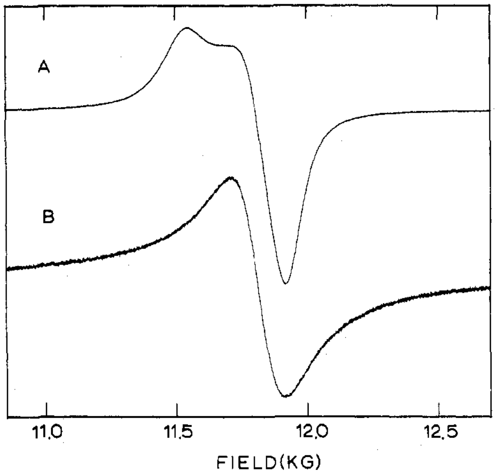

Figure 6. Room-temperature Q-band EPR spectra of powdered samples of $[Cu_2(bpy)_4(CN)](PF_6)_3$ (A) and $[Cu_2(tren)_2(CN)](PF_6)_3$ (B).

The bipyridine compound shows two features, a "bump" at $g = 2.165$ and a derivative crossing the baseline at $g = 2.118$. A monomeric $Cu(bpy)_2X^+$ complex would be expected to be trigonal bipyramidal and to show an EPR spectrum similar to those illustrated in Figure 5 for the $Cu(phen)_2(CN)^+$ species. Thus, the spectrum for $[Cu_2(bpy)_4(CN)](PF_6)_3$ is also unusual.

The X-band EPR spectra of all three of our cyanide dimers are shown in Figure 7. It can be seen that each spectrum essentially consists of a single derivative at $g \simeq 2.1$. The spectrum (tracing A) of the phenanthroline compound also shows two low-intensity signals ($g = 2.642$ and 1.828) on either side of the main signal. These two low-intensity features could be due to an impurity, since the initially obtained powder gives

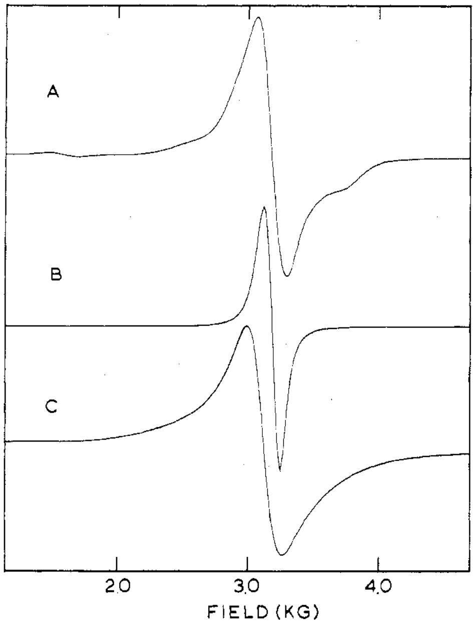

Figure 7. Room-temperature X-band EPR spectra of powdered samples of $[Cu_2(phen)_4(CN)](PF_6)_3$ (A), $[Cu_2(bpy)_4(CN)](PF_6)_3$ (B), and $[Cu_2(tren)_2(CN)](PF_6)_3$ (C).

a spectrum where these two features are more pronounced than in the spectrum (Figure 7, tracing A) for a sample obtained by powdering single crystals. It is interesting to note that the X-band spectrum (tracing B) of $[Cu_2(bpy)_4(CN)](PF_6)_3$ shows the narrowest derivative, in contrast to the two features seen in the Q-band spectrum (tracing A in Figure 6).

Additionally, $\Delta M_s = 2$ transitions are seen for all three compounds in the X-band spectra. The "forbidden" $\Delta M_s = 2$ transition for the phenanthroline compound is so intense that it can be seen with the same gain setting as is needed for the $\Delta M_s = 1$ transition (see Figure 7). The intensity of a $\Delta M_s = 2$ transition is dependent on the magnitude of zero-field splitting in the triplet. Zero-field splitting can be both dipolar and pseudodipolar in origin. The former leads to a dependence of zero-field splitting on Cu–Cu distance and **g** tensor/**D** tensor orientation and the latter depends on exchange interactions in excited states. The fact that the $\Delta M_s = 2$ transitions are of different relative intensities for the phenanthroline and bipyridine dimers probably means there is a difference in **g** tensor/**D** tensor nonalignment for the two dimers.

A detailed explanation of the EPR spectra of our three cyanide dimers will have to await x-ray structural work; however, a qualitative discussion of the important factors can be presented. Abragam and Bleaney[19] have discussed the EPR expected for a pair of dissimilar $S = \frac{1}{2}$ metal ions that are involved in an isotropic magnetic exchange interaction. For the sake of simplicity, they assumed that the principal axes of the two **g** tensors are identical, but the principal g values are not. Only the z component of each **g** tensor was considered (i.e., isotropic **g** tensor for each ion). With these assumptions, the Hamiltonian operator has the form

$$\hat{H} = \beta H_z(g_{iz}\hat{S}_{iz} + g_{jz}\hat{S}_{jz}) - 2J\hat{S}_i\cdot\hat{S}_j$$

When there is no exchange interaction, $J = 0$ and two resonances are seen, one at g_i and the other at g_j. They further showed that, as J becomes nonzero and increases over a range of the order of the energy difference between the g_i and g_j resonances, then the original signals split into two doublets, the components of each doublet being separated approximately by an amount $2J$. As J increases, the splitting in each doublet increases. The two resonances at either high or low field lose intensity, while the other two resonances converge to an average field position with $g = \frac{1}{2}(g_i + g_j)$. The two converging resonances, one from each of the original doublets, gain in intensity as J increases. Finally, when J greatly exceeds the difference in frequencies of the two original resonances at g_i and g_j, then only one resonance is seen at a g value of $\frac{1}{2}(g_i + g_j)$. Thus, the resonances for the two dissimilar ions are exchange averaged to one resonance.

One example of the effects of magnetic exchange in a "dissimilar" ion pair can be drawn from EPR studies[20,21] of $CuSO_4{\cdot}5H_2O$. The x-ray structure[22] of this compound shows that there are two crystallographically inequivalent ions in a unit cell. The extended lattice consists of Cu(II) ions, each in a tetragonally distorted octahedral environment of four water molecules and two oxygen atoms from bridging sulfate ions. The exchange interaction (frequency) of 0.15 cm^{-1} (estimated) leads to the observation of *one* absorption line at microwave frequencies of 9.88 and 24.4 GHz. The frequency of electron exchange in $CuSO_4{\cdot}5H_2O$ is of such a magnitude that with a higher microwave frequency of 35.3 GHz *two* absorption lines are seen. Thus, when the exchange interaction is weak enough, it is possible to select a microwave frequency that is greater than the frequency of electron exchange between the two dissimilar ions and this allows one to see the separate signals.

The exchange interactions (−9.4, −29, and −88 cm^{-1}) in our three cyanide-bridged Cu(II) dimers, as well as that (−4.8 cm^{-1}) seen[8] for $[Cu_2([14]4,11\text{-diene-}N_4)_2(CN)](ClO_4)_3$, are much greater than was found for $CuSO_4{\cdot}5H_2O$. The frequency at which electrons are exchanging between the two dissimilar Cu(II) ions in these cyanide-brdiged dimers would be expected to be much greater than either the X- or Q-band microwave frequencies that we used in our EPR measurements and we would expect that the above EPR spectra are exchange averaged. If we assume that, in the Cu–CN–Cu dimer, the components of the **g** tensors at either the carbon-bonded Cu(II) ion or the nitrogen-bonded Cu(II) ion are approximately the same, it is possible to explain the above observed EPR spectra. The x-ray structure[8] of $[Cu_2([14]4,11\text{-diene-}N_4)_2(CN)](ClO_4)_3$ shows that the cyanide-bridged dimer is situated on a center of inversion. Rapid electron exchange in this dimer would only average the x_i and x_j components of the **g** tensor, the y_i and y_j components, and the z_i and z_j components. The averaged **g** tensor for the dimer could look like a somewhat broadened monomer spectrum.

The structures of the other three cyanide-bridged dimers are, of course, unknown. However, if in each case there is *not* a center of inversion in the dimer, the exchange averaging will produce more dramatic effects. It is relevant to point out that the x-ray structure[7] of $(NC)_5Co{-}CN{-}Co(NH_3)_5{\cdot}H_2O$ shows that the Co–CN–Co moiety is not linear, but has angles of CoCN = 172.4° and CNCo = 159.8°, respectively. In such a nonlinear array, all of the components of each of the two **g** tensors can be averaged. This would give a single average resonance as is seen for all three of our compounds except $[Cu_2(bpy)_4(CN)](PF_6)_3$. For this last compound, it still remains to explain why two resonances are seen at Q-band frequency, whereas only one relatively narrow resonance is seen at X-band frequencies. This could be simply due to differences in resolution of X-band vs. Q-band EPR for nearby signals. Single-crystal EPR work would be enlightening and interesting.

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Registry No. $[Cu_2(phen)_4(CN)](PF_6)_3$, 61723-50-0; $[Cu_2(bpy)_4(CN)](PF_6)_3$, 61723-52-2; $[Cu_2(tren)_2(CN)](PF_6)_3$, 61651-92-1;

$[Cu(phen)_2(CN)]NO_3$, 42741-08-2; $[Cu(phen)_2(CN)]PF_6$, 61723-53-3.

Supplementary Material Available: Tables I–III showing calculated and observed magnetic susceptibility data (4 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Camille and Henry Dreyfus Fellowship, 1972–1977; A. P. Sloan Fellowship, 1976–1978.
(2) A. Ludi and H. U. Güdel, *Struct. Bonding (Berlin)*, **14**, 1 (1973).
(3) A. H. Norbury and A. I. P. Sinha, *Q. Rev., Chem. Soc.*, **24**, 69 (1970).
(4) D. F. Shriver, *Struct. Bonding (Berlin)*, **1**, 32 (1966).
(5) D. Britton, *Perspect. Struct. Chem.*, **1**, 109 (1967).
(6) B. M. Chadwick and A. G. Sharpe, *Adv. Inorg. Chem. Radiochem.*, **8**, 83 (1966); A. G. Sharpe, "The Chemistry of Cyano Complexes of the Transition Metals", Academic Press, New York, N.Y., 1976.
(7) B.-C. Wang, W. P. Schaefer, and R. E. Marsh, *Inorg. Chem.*, **10**, 1492 (1971).
(8) D. M. Duggan, R. G. Jungst, K. R. Mann, G. D. Stucky, and D. N. Hendrickson, *J. Am. Chem. Soc.*, **96**, 3443 (1974).
(9) D. M. Duggan and D. N. Hendrickson, *Inorg. Chem.*, **13**, 2929 (1974).
(10) J. P. Chandler, Program 66, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.
(11) E. J. Laskowski, D. M. Duggan, and D. N. Hendrickson, *Inorg. Chem.*, **14**, 2449 (1975).
(12) D. M. Duggan and D. N. Hendrickson, *Inorg. Chem.*, **13**, 1911 (1974).
(13) D. A. Dows, A. Haim, and W. K. Wilmarth, *J. Inorg. Nucl. Chem.*, **21**, 33 (1961).
(14) O. P. Anderson, *Inorg. Chem.*, **14**, 730 (1975).
(15) B. Bleaney and K. D. Bowers, *Proc. R. Soc. London, Ser. A*, **214**, 451 (1952).
(16) A. P. Ginsberg, *Inorg. Chim. Acta, Rev.*, **5**, 45 (1971).
(17) B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, **5**, 143 (1970).
(18) W. H. Morrison, Jr., and D. N. Hendrickson, *Inorg. Chem.*, **11**, 2600 (1972).
(19) A. Abragam and B. Bleaney, "Electron Paramagnetic Resonance of Transition Ions", Clarendon Press, Oxford, 1970, p 509–514.
(20) D. M. S. Bagguley and J. H. E. Griffiths, *Proc. R. Soc. London, Ser. A*, **201**, 366 (1950).
(21) K. Ono and M. Ohtsuka, *J. Phys. Soc. Jpn.*, **13**, 206 (1958).
(22) C. A. Beevers and H. Lipson, *Proc. R. Soc. London, Ser. A*, **146**, 570 (1934).

Contribution from the Department of Inorganic Chemistry,
The University of Melbourne, Parkville 3052, Australia

Volumes of Activation for Intramolecular Racemization Mechanisms. High-Pressure Racemization of Bipyridyl, Phenanthroline, and Oxalato Complexes of Chromium(III) in Solution

G. A. LAWRANCE and D. R. STRANKS*

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The effect of high pressure on the rates of racemization of metal complexes in solution has been evaluated for the first time. The racemization of $Cr(phen)_3^{3+}$ exhibits a volume of activation, $\Delta V^{\ddagger} = +3.3 \pm 0.2$ cm^3 mol^{-1}, which is shown to be consistent with an intramolecular twist mechanism. The racemization of $Cr(C_2O_4)_3^{3-}$ exhibits $\Delta V^{\ddagger} = -16.3 \pm 0.4$ cm^3 mol^{-1}, consistent with racemization through one-ended dissociation of an oxalato ligand. $Cr(phen)(C_2O_4)_2^-$ and $Cr(bpy)(C_2O_4)_2^-$ exhibit $\Delta V^{\ddagger} = -12.3 \pm 0.3$ and $\Delta V^{\ddagger} = -12.0 \pm 0.3$ cm^3 mol^{-1}, respectively, and these racemizations are assigned a one-ended dissociation mechanism. $Cr(phen)_2(C_2O_4)^+$, $Cr(bpy)_2(C_2O_4)^+$, and $Cr(bpy)_3^{3+}$ exhibit $\Delta V^{\ddagger} = -1.5 \pm 0.2$, −1.0 [illegible] 0.1, and $+3.4 \pm 0.3$ cm^3 mol^{-1}, respectively, and these are all assigned intramolecular twist mechanism. Enthalpies and entropies of activation were evaluated for all of these systems; $\Delta H^{\ddagger}$ values are least for $Cr(C_2O_4)_3^{3-}$ and greatest for $Cr(phen)_3^{3+}$ and $Cr(bpy)_3^{3+}$ while $\Delta S^{\ddagger}$ values, all large and negative, show the reverse trend.

Introduction

Both intermolecular and intramolecular mechanisms have been proposed for racemization and isomerization in six-coordinate octahedral chelate complexes, and recent studies to elucidate these mechanisms have been the subject of a recent extensive review.[1] The intermolecular mechanism, involving complete loss of one chelate ligand, may be detected by isotopic exchange studies and by comparison of dissociation or aquation rates with those for isomerization or racemization. However, the elucidation of intramolecular mechanisms is more difficult even though extensive information has accumulated from exchange studies and from measured enthalpies and entropies of activation. A new approach which we are now proposing is to study the effect of high pressure upon the rates of racemization in solution to evaluate the volume of activation, $\Delta V^{\ddagger}$, for the racemization process. Each of the possible intramolecular mechanisms may then be considered in terms of the difference in volume of the transition state for the racemization and the corresponding ground state. This approach has been fruitful in elucidating details of inorganic substitution and redox reactions[2,3] and similar interpretative approaches should apply to racemization processes.

Two essentially different types of intramolecular mechanism have been proposed for complexes of bidentate ligands and are differentiated by whether racemization occurs with or without bond rupture. The bond-rupture mechanism was first proposed by Werner[4] and involves a *one-ended dissociation* of a bidentate ligand from the central metal ion. This dissociative process is accompanied by rearrangement of the remaining groups to a five-coordinate transition state which would have either the limiting trigonal-bipyramidal (I) or the square-pyramidal (II) structure. This rearrangement must involve motion or twisting of at least one of the intact chelate rings. Reattachment of the dangling ligand and reversion to an octahedral configuration may occur at the identical site to that

Scheme I