value over quite a wide range, and the positions of these levels were therefore calculated using an approximate value of $B \approx 500\ \text{cm}^{-1}$ (based on the solution data) and the other parameters as shown in Table I. It is seen that the calculated energies are somewhat smaller than the photoelectron results indicate and, although it is not clear why this should be so, the qualitative agreement is not unreasonable, and the proposed assignment is much more consistent with the ligand field treatment than that previously suggested.[14]

For the d^5 system, Mn(Cp)$_2$, a high-spin $^6\Sigma^+$ ($\sigma\pi^2\delta^2$) ground state is normally assumed on the basis of the magnetic moment of 5.92 BM found for solid samples.[15] Furthermore, esr measurements[16] yield an almost isotropic *g* value of 1.99-2.01 which is also consistent with a $^6\Sigma^+$ ground state, although the low-spin $^2\Sigma^+$ ($\sigma\delta^4$) cannot be ruled out. Nevertheless, Rabelais, *et al.*,[14] concluded that in the gas phase the ground state is low spin and that it actually is $^2\Sigma^+$ ($\sigma\delta^4$) rather than the $^2\Delta$ ($\sigma^2\delta^3$) ground state found[6] for the isoelectronic Fe(Cp)$_2^+$. They argued that on ionization to the d^4 ion Mn(Cp)$_2^+$ a $^2\Sigma^+$ ($\sigma\delta^4$) state gives rise to the δ^4 and $\sigma\delta^3$ configurations corresponding to the states $^1\Sigma^+$ (δ^4), $^3\Delta$ ($\sigma\delta^3$), and $^1\Delta$ ($\sigma\delta^3$), and these levels were equated with the three closely grouped components into which they resolved the first photoelectron band (see Table I). However, as indicated in Figure 1, for any reasonable parameter choice $^1\Sigma^+$ (δ^4) will always lie substantially above $^3\Delta$ ($\sigma\delta^3$), usually to the extent of some 2 eV, so that the proposed assignment cannot be maintained. On the other hand the ligand field calculations of Sohn, Hendrickson, and Gray,[6] indicate that for a low-spin d^5 system, $^2\Delta$ ($\sigma^2\delta^3$) will normally lie lowest and that the $^2\Sigma^+$ ($\sigma\delta^4$) state would only become the ground level at very high Dt/B values. Thus for a $^2\Delta$ ($\sigma^2\delta^3$) ground state the d^4 configurations δ^3 and $\sigma^2\delta^2$ would arise on ionization, leading to the states (in ascending energetic order) $^3\Delta$ ($\sigma\delta^3$), $^3\Sigma^-$ ($\sigma^2\delta^2$), $^1\Gamma$, $^1\Sigma^+$ ($\sigma^2\delta^2$), and $^1\Delta$ ($\sigma\delta^3$), the first three therefore being possible components of the first photoelectron band. Unfortunately, Mn(Cp)$_2^+$ is not known in solution but interpolated values of Ds, Dt, and B suggest that $^3\Sigma^-$ and $^1\Gamma$, $^1\Sigma^+$ lie respectively about 0.2 and 0.7 eV above $^3\Delta$. Thus the energy separation for the $^3\Sigma^-$ ($\sigma^2\delta^2$) level is of the right order of magnitude to support this assignment, but the calculated energy difference for the $^1\Gamma$, $^1\Sigma^+$ levels is appreciably greater than the observed value. Moreover, a further band about 1 eV above $^3\Delta$ ($\sigma\delta^3$) is also predicted corresponding to the $^1\Delta$ ($\sigma\delta^3$) level, but the photoelectron spectrum shows no evidence of this.

If therefore Mn(Cp)$_2$ is in fact low-spin, it clearly cannot possess a $^2\Sigma^+$ ($\sigma\delta^4$) ground level according to the above interpretation of the photoelectron spectrum. A $^2\Delta$ ($\sigma^2\delta^3$) ground level is more consistent with the experimental data, but here one band appears at much lower energy than anticipated, and another is missing altogether. On the other hand though, the He(I) spectra appear to exclude the possibility of a high-spin ground level: on ionization the $^6\Sigma^+$ ($\sigma\pi^2\delta^2$) state would give rise to the configurations $\pi^2\delta^2$, $\sigma\pi^2\delta$, and $\sigma\pi\delta^2$, of which the last proves to lead to the lowest energy states for the parameter range considered here. In fact the $^5\Pi$ ($\sigma\pi\delta^2$) state will lie some 1.2 eV below the next lowest $\sigma\pi\delta^2$ levels—four closely juxtaposed states, $^3\mathrm{H}$, $^3\Phi$, $^3\Pi$, and $^3\Pi$—but photoionization to these should not take place from a sextet ground level[17] since the coefficients of fractional parentage which connect them are necessarily zero. The higher lying quintet levels, $^5\Sigma^+$ ($\pi^2\delta^2$) and $^5\Delta$ ($\sigma\pi^2\delta$), to which transitions are possible, will lie at 1.5-2.25 and at 1.9-2.9 eV, respectively, above $^5\Pi$ for the Dt/B range 3.0-4.5, assuming $Dt/Ds = 0.55$, which again is not consistent with the reported photoelectron results.

However, one possible interpretation would be to regard the three reported components of the first photoelectron band as arising from incompletely resolved vibrational structure rather than from separate electronic states. The first band could then be assigned as being due to the $^5\Pi$ ($\sigma\pi\delta^2$) level and the broad band found between 1.2 and 2.6 eV ascribed either to the $^5\Sigma^+$ ($\pi^2\delta^2$) and $^5\Delta$ ($\sigma\pi^2\delta$) states or to excitations involving dominantly ligand orbitals, as suggested by Rabelais, *et al.*,[14] for bands of similar energy found for this and other metallocenes. It is thus a feasible alternative to assign the photoelectron data on the basis of a $^6\Sigma^+$ ground state, and although it is not possible to decide between the two explanations in the absence of further experimental evidence, it is hard to believe that Mn(Cp)$_2$ is high spin in the solid state and low spin in the gas phase. Moreover, recent INDO-type molecular orbital calculations[12] show the $^6\Sigma^+$ level to be appreciably more stable than either of the doublet configurations.

Finally, the d^4 repulsion matrices are also of value for the treatment of the complementary d^6 systems, of which many examples (*e.g.*, Fe(Cp)$_2$) are known. However, the partial results including all the singly excited states have already been given,[6] and the inclusion of the higher excited levels has usually only a minor effect on the fitting parameters.

Registry No. Mn(Cp)$_2^+$, 50803-41-3; Cr(Cp)$_2^+$, 12793-15-6.

Supplementary Material Available. The Appendix will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-1243.

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Contribution from the Department of Chemistry,
University of North Carolina, Chapel Hill, North Carolina 27514

Magnetic Properties of Di-μ-chloro-bis[dichloro(guaninium)copper(II)] Dihydrate. A Second Determination[1]

Robert F. Drake, Van H. Crawford, Nancy W. Laney, and
William E. Hatfield*

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In 1970 Carrabine and Sundaralingam reported the structure of di-μ-chloro-bis[dichloro(guaninium)copper(II)]

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(1) Subsequent to the submission of a complete paper on the magnetic properties of this compound, an article describing similar measurements appeared.[2] While we basically are in agreement with Villa's conclusions, our more extensive measurements have permitted a more precise determination of the singlet-triplet splitting.

(2) J. F. Villa, *Inorg. Chem.*, **12**, 2054 (1973).

dihydrate.[3] The guaninium ligand is the name given to the cation formed by monoprotonating guanine, one of the bases bonded to the sugar residues in the backbone of deoxyribonucleic acid (DNA). The same authors presented a more complete structural analysis the following year,[4] and the structure was then confirmed by Declercq, Debbaudt, and Van Meerssche in an independent investigation.[5] Both research groups reported the structure to be that of a dimer consisting of chloro-bridged, trigonal-bipyramidally coordinated copper(II) ions, as shown in Figure 1. The monoprotonation was shown to occur at the imidazole nitrogen, N(7), of the purine ring system, and binding to the copper ion, at N(9). The bridging Cu-Cl distances were determined to be 2.447 and 2.288 Å, with a Cu-Cl-Cu bridging angle of 98° and a Cu-Cu separation of 3.575 Å. Since magnetic studies of the complex tris(ethylenediamine)cobalt(III) di-μ-chloro-bis[trichlorocuprate(II)][6,7] chloride have revealed the presence of an exchange interaction between copper(II) ions, and since the bridging unit in the $[Cu_2Cl_8]^{4-}$ anion has been shown[8] to be structurally similar to that reported for the guaninium complex, it was anticipated that an exchange interaction might also be present in the guaninium complex. A study of the magnetic properties of $[(\text{guaninium})CuCl_3]_2 \cdot 2H_2O$ was undertaken, and the results are described in this paper.

Experimental Section

The complex was prepared by the method of Sundaralingam and Carrabine.[4] *Anal.* Calcd for $[(C_5H_6N_5O)CuCl_3] \cdot H_2O$: C, 17.66; H, 2.37; N, 20.59. Found: C, 17.74; H, 2.29; N, 20.40. Magnetic susceptibility data were obtained for a powder sample over the temperature range 1.6 to 255°K using a Foner-type[9] vibrating sample magnetometer[10] mounted on a Magnion electromagnet with rotating gaussmeter probe. The field was calibrated at 10,000 G using a Magnion nmr precision gaussmeter (Li resonance). The magnetometer was calibrated using the magnetic susceptibility standard $HgCo(NCS)_4$.[11] The temperature in the cryostat was measured using a calibrated gallium arsenide diode sensor[12] coupled to a 10 μA constant current source[13] and monitored with a 4.5-place digital voltmeter.[14] All susceptibility data were corrected for the diamagnetism of constituent atoms using Pascal's constants[15] and for temperature-independent paramagnetism (TIP) according to the expression TIP = $N\Delta g\beta^2/\lambda = 60 \times 10^{-6}$ cgsu.[16]

The epr spectrum of the guaninium complex was obtained at 77.3°K using a Varian E-3 spectrometer. The electromagnet of the spectrometer was calibrated using nmr techniques.

Results

The temperature variation of the inverse susceptibility

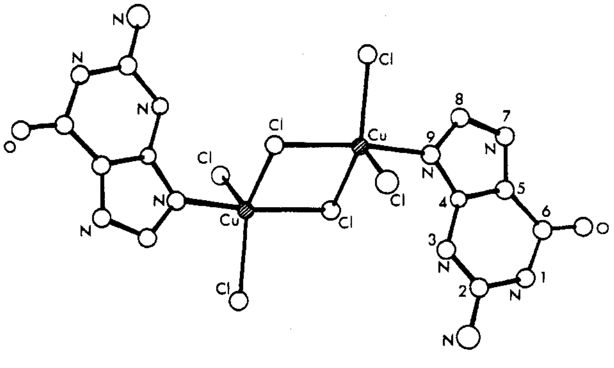

Figure 1. The structure of di-μ-chloro-bis[dichloro(guaninium)-copper(II)] dihydrate. Unlabeled atoms are carbon atoms. (Adapted from ref 3.)

(calculated per copper(II) ion) of a powdered sample in the temperature region 1.6 to 255°K is represented by the black data points in Figure 2. The maximum in the curve occurring at approximately 15°K is probably due to a small percentage of monomeric impurity which did not affect the percentage composition of the elemental analysis. To correct for this impurity, the data points from 1.6 to 11.2°K were fit to the Curie-Weiss law, eq 1, and values were ob-

$$\chi = C/(T - \Theta) \qquad (1)$$

tained for the constants C and Θ of 7.86×10^{-3} and $-3.22°$, respectively. In this temperature region the susceptibility of the dimer is negligibly small (*vide post*). All the data points were then corrected for the contribution of the impurity to the observed susceptibility, and the corrected points are also plotted in Figure 2 as the open circles. The impurity was estimated to be present to the extent of 1% in the following way: The susceptibility for an assumed monomer having a molecular weight equal to one-half that of the dimer was calculated from the expression[17]

$$\chi = N\beta^2\mu^2/3kT \qquad (2)$$

where $\mu = g\beta[S(S + 1)]^{1/2}$, at a selected temperature, and the calculated susceptibility was compared with the experimental susceptibility at that temperature. A similar correction to the susceptibility of the complexes $[(CH_3)_4N]_4[Cu_4OCl_{10}]$ and $[(C_6H_5)_3PO]_4[Cu_4OCl_6]$ was applied by Lines, *et al.*[18]

The epr spectrum of the powder sample of $[(\text{guaninium})CuCl_3]_2 \cdot 2H_2O$ is shown in Figure 3. The spectrum is poorly resolved due to dipolar interactions which are caused by the significant population of the triplet excited state at 77.3°K, but, even so, the "half-field" line from the $\Delta M_S = \pm 2$ transition of a typical triplet species may be seen near 1500 G. There also is an absorption near 4000 G which was not noticed by Villa[2] and which is probably due to the high field parallel transition,[19] and there is a broad unsymmetrical band at approximately 3000 G which envelops the other triplet state transitions. Assignment of resonance fields is made impossible by the broadening of the spectrum and by the presence of monomeric impurities (*vide supra*). Low-temperature (~10°K) epr studies should aid in obtaining an interpretable spectrum since the population of the triplet

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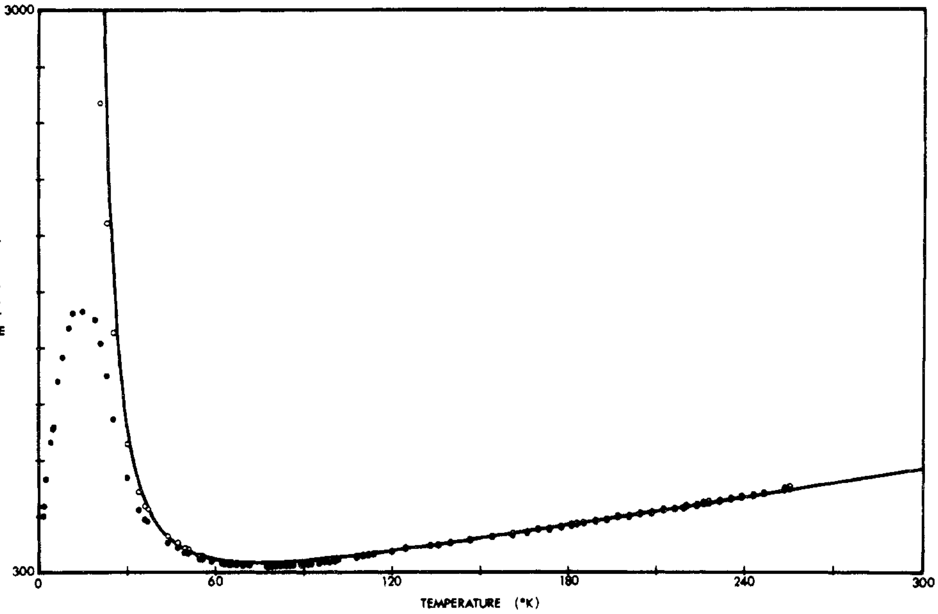

Figure 2. Temperature *vs.* inverse susceptibility plot for the complex [(guaninium)CuCl$_3$]$_2$·2H$_2$O. Experimental points (●); experimental points corrected for monomeric impurity (○); Van Vleck equation best fit (—).

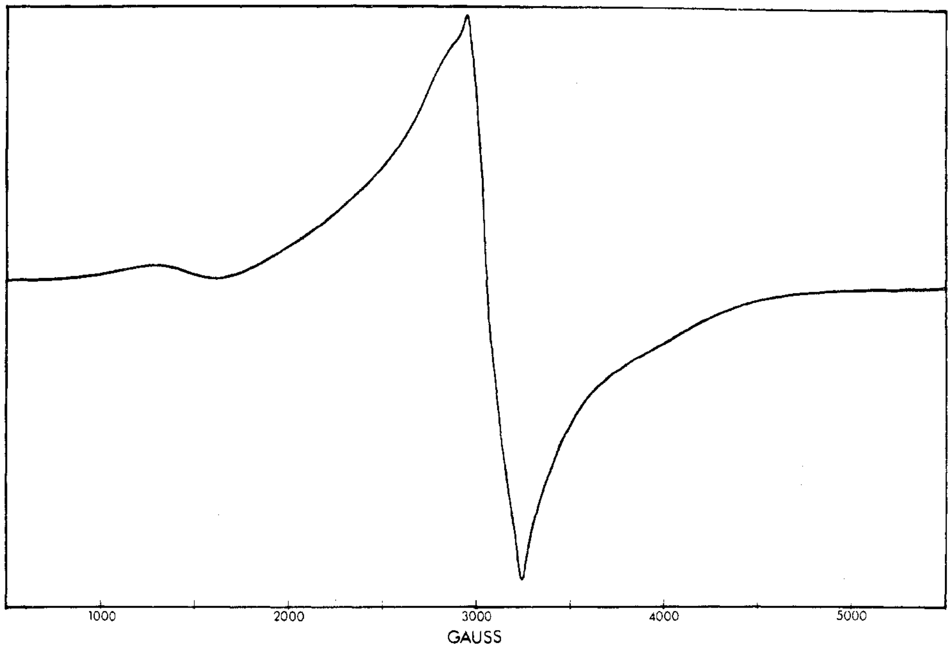

Figure 3. Epr spectrum (9.358 GHz) of the complex [(guaninium)CuCl$_3$]$_2$·2H$_2$O at 77.3°K.

state will be very small at such a low temperature and the effects of dipolar broadening will be minimized.

Discussion

The solid curve in Figure 2 is the best fit of the corrected data to the modified Van Vleck equation (eq 3)[20-23] for

$$\chi_M = \frac{Ng^2\beta^2}{3k(T-\Theta)}[1 + (^1/_3)\exp(-2J/kT)]^{-1} + N\alpha \qquad (3)$$

exchange-coupled copper(II) dimers, which results from a consideration of the eigenvalues of (4), the Heisenberg ex-

$$\mathcal{H} = -2JS_1 \cdot S_2 \qquad (4)$$

change Hamiltonian. The symbols in (3) have their usual meanings. The parameter Θ accounts for the interdimer coupling of spins throughout the lattice. Computation of the best fit was obtained using a computer program which varies values of $2J$ and g in a least-squares, best-fit procedure. The criterion used to determine the best fit is the minimization of the sum of the squares of the deviation, A, where

$$A = \sum_i (\chi_i^{\text{calcd}} - \chi_i^{\text{exptl}})^2 T_i^2 \qquad (5)$$

The weighting of the susceptibility values by the temperature is necessary in order to prevent overemphasis of the low-temperature points, where the magnitude of the susceptibility values are much greater than at higher temperatures. The following parameters were extracted from the data: $2J = -82.6 \pm 1.0$ cm^{-1} and $g = 2.12 \pm 0.02$. Thus, the spin-

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Table I. Magnetic and Structural Data for Chloro-Bridged Copper(II) Dimers

Complex	$2J$, cm^{-1}	Structure	Cu-Cl-Cu angle, deg	Cu-Cl bond, Å In-plane	Out-of-plane	Ref
$[(\text{Guaninium})\text{CuCl}_3]_2 \cdot 2\text{H}_2\text{O}$	−82.6	Trigonal bipyramidal	98	2.45	2.29	3-5, this work
$[\text{Cu}_2\text{Cl}_8]^{4-}$ anion	−14.6	Trigonal bipyramidal	95.2	2.70	2.33	6-8
$[(\text{2-Me(py)})_2\text{CuCl}_2]_2$ [a]	−7.4	Square pyramidal	101.4	2.26	3.37	29, 30
$[(\text{DMG})\text{CuCl}_2]_2$ [b]	+6.3	Square pyramidal	88	2.24	2.70	31, 32

[a] 2-Me(py) = 2-methylpyridine. [b] DMG = dimethylgloxime.

spin interaction results in a singlet ground state for the dimer with an excited triplet about 83 cm^{-1} higher in energy. In view of the more extensive data reported herein, this value is more precise than the value reported previously.[2]

It should be noted that the introduction of nonzero values for Θ did not improve the fit of eq 3 to the experimental data. This indicates that there is no significant interdimer exchange, a result not unexpected in light of the molecular packing of the dimers in the crystalline state.

The large Cu-Cu separation of 3.575 Å precludes through-space interactions between these metal ions since orbital overlap over this distance is extremely small, and dipolar interactions could not produce a splitting of the magnitude observed. It must be concluded, therefore, that the interaction occurs *via* superexchange through the chloride bridges.

It is of interest to compare the magnetic parameters and structural data for the guaninium complex with comparable data for the other structurally and magnetically characterized chloro-bridged bimetallic copper(II) complexes known at this time. These data are compiled in Table I. Both the guaninium complex and the $[\text{Cu}_2\text{Cl}_8]^{4-}$ anion mentioned previously are made up of trigonal bipyramids sharing equatorial-to-apex edges, while the other two complexes listed in the table are square-based pyramids sharing base-to-apex edges. In the trigonal-bipyramidal complexes, it is likely that the unpaired electrons are in the d_{z^2} orbitals of the copper(II) ions in the ground state, whereas in the square-pyramidal complexes it is likely that they are in the $d_{x^2-y^2}$ orbitals. A quantitative comparison of the exchange energies of the four complexes cannot be based on structural data because of the different orbitals involved in superexchange, but a qualitative comparison is possible.

The structural parameters of the guaninium complex and the $[\text{Cu}_2\text{Cl}_8]^{4-}$ anion are compared by superimposition in Figure 4 with the solid line representing the guaninium complex. The smaller singlet-triplet splitting for the $[\text{Cu}_2\text{Cl}_8]^{4-}$ anion in comparison to the guaninium complex accompanies an increase in the Cu-Cl-Cu bond angle from 95 to 98° and a decrease in the bridging bond lengths. Although it has been demonstrated that the bridging angle is important in determining the sign and magnitude of the splitting parameter $2J$ in a series of hydroxo-bridged copper(II) complexes,[24] it is unlikely this effect can be presented as the sole explanation in this comparison because the bridging bond lengths of these two chloro-bridged species are quite different, ranging between 2.3 and 2.7 Å, whereas they are nearly constant in the hydroxo-bridged species[25-28] at 1.90 to 1.94 Å.

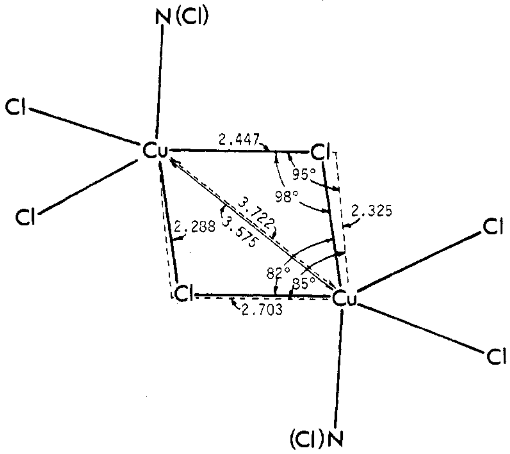

Figure 4. Comparison of the structural parameters for $[(\text{guaninium})\text{CuCl}_3] \cdot 2\text{H}_2\text{O}$ and $[\text{Cu}_2\text{Cl}_8]^{4-}$, with the solid line representing the guaninium complex.

The complexes $[(\text{2-Me(py)})_2\text{CuCl}_2]_2$ and $[(\text{DMG})\text{CuCl}_2]_2$ have different structures and different exchange coupling mechanisms.[29-32] In comparing these two square-pyramidal complexes, it should be noted that there is a change in ground state multiplicity. The bridging bond length in $[(\text{2-Me(py)})_2\text{CuCl}_2]_2$ is 0.67 Å longer than the comparable bond in $[(\text{DMG})\text{CuCl}_2]_2$ and the angle at the bridging chloride is 13.4° larger in the 2-methylpyridine complex than in the dimethylglyoxime complex. It is, therefore, not possible to attribute the change in the exchange coupling constant only to bridge angle changes.

Clearly a number of additional chloro-bridged copper(II) dimers of both structural configurations must be studied before the bridge-angle effect on $2J$ can be separated from the bridging bond-length effect.

Acknowledgments. This research was supported by the National Science Foundation through Grant GP-22887 and the Materials Research Center of the University of North Carolina under Grant No. GH-33632 from the National Science Foundation. We wish to thank Mr. Kenneth T. McGregor for helpful discussions.

Registry No. $[(\text{Guaninium})\text{CuCl}_3]_2 \cdot 2\text{H}_2\text{O}$, 27679-78-3.

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