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Electronic Studies of Copper(II) Complexes of Nucleic Acid Bases. IV. Ground State and Electronic and Spin Arrangement in Trichloroguaniniumcopper(II) Monohydrate¹

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A complete spectral and magnetic study was carried out on trichloroguaniniumcopper(II) monohydrate. The electronic spectrum of this pseudo- D_{3h} symmetry molecule indicated an A' ground state at approximately -7600 cm^{-1} , while epr and magnetic susceptibility measurements indicated the presence of spin interactions with a spin-singlet ground state and a spin-triplet state 99 cm^{-1} higher.

Introduction

The important role of transition metal ions in biological processes is now well established.^{2,3} The metalloenzymes are a good example of known biological activity of transition metal ions.⁴⁻⁶ Other examples are the transamination process of vitamin B₆, the respiration process, and even cases of severe physiological abnormalities such as the Wilson disease have^{7,8} been shown to be dependent on the "miscoordination" of these ions. Another area of importance has been investigated by Eichhorn and coworkers among others; this is the interaction of transition metal ions with DNA, RNA, and their constituent nucleotides, nucleosides, and bases.^{9,10} The present report is representative of this area of research.

It is an established fact that RNA is denatured by the presence of transition metal ions such as Zn(II) and Cu(II).¹¹ The reaction seems to be rather specific, with binding sites at the N(7) of the bases and PO₄ groups, and also reversible with helix reformation after removal of the transition metal ions. There are also reports of coordination compounds of transition metal ions¹² with mononucleotides and just recently a few compounds with nucleosides have been reported in solution.¹³

The bases that form part of DNA and RNA are also usually reactive toward transition metal ions. Of particular interest are the guanine and adenine derivatives that have been shown to form dimers in the solid state¹⁴⁻¹⁶ and that have the unus-

ual cationic form of these compounds as ligands.¹⁷ We report here a complete magnetic and spectral study of trichloroguaniniumcopper(II) monohydrate, Cu(gua)Cl₃·H₂O, the structure of which¹⁵ is shown in Figure 1. Note that two chloride ions act as bridges between the two copper(II) ions in the dimeric structure. The Cu-Cu distance is about 3.7 Å and the guaninium ion is protonated at N(3) and N(7) and coordinated *via* N(9). Also, the coordination around the copper(II) is of approximately D_{3h} symmetry and similar to those of the CuCl₅³⁻ systems.¹⁸

Experimental Section

The compound was prepared similarly to the method of Sundaralingam,¹⁵ as follows. A fourfold excess of CuCl₂·2H₂O (1.36 g) was dissolved in aqueous HCl (2 M) with the formation of a light yellow solution. To this, guanine was added (0.3 g) and the mixture was vigorously stirred with heat until all the guanine was dissolved. Concentrated HCl was added until the solution changed color to a dark green and then was evaporated down to one-third the volume (20 ml). Upon cooling, yellow-brown crystals appeared which could be easily filtered. *Anal.* Calcd for Cu(C₅H₆N₅O)Cl₃·H₂O: C, 17.65; H, 2.37; N, 20.60. Found: C, 17.65; H, 2.44; N, 20.64.

The epr spectra were obtained at 295 and 77°K in a Varian E-3 spectrometer using X-band frequencies and polycrystalline DPPH as a field marker.¹⁹ The magnetic susceptibility was obtained in the temperature range 300-77°K using a Faraday balance setup and HgCo-(NCS)₄ as the standard, and below 77°K using a Foner-type, vibrating-sample magnetometer from Princeton Applied Research, Inc.²⁰ The appropriate diamagnetic corrections were made including 2×10^{-6} /mol for the compound itself calculated using Pascal's constants²¹ and a TIP correction of 1×10^{-6} /mol. The electronic spectra were obtained with a Beckman DK-2A spectrophotometer in the 400-1500-nm range as Nujol mulls pressed between quartz plates. The analyses were carried out by Galbraith Laboratories, Inc. Several Fortran IV programs and an IBM 360-40 computer were used in data reduction and simulation.

Results and Discussion

Electronic Spectrum. The visible-near infrared spectrum of Cu(gua)Cl₃·H₂O can be interpreted in terms of a D_{3h} symmetry coordination around the Cu(II) ion, with three chloride ions in the equatorial plane and one chloride ion and the guaninium molecule in the axial position. This yields a splitting into three states, $A'(d_z^2)$, $E'(d_{x^2-y^2}, d_{xy})$, and $E''(d_{xz}, d_{yz})$, with two possible electronic transitions, $A' \rightarrow E'$ and $A' \rightarrow E''$. These bands are observed in our case at 8000 and 10,500 cm^{-1} , respectively. These assignments are in agree-

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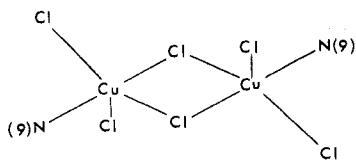


Figure 1. Structure of trichloroguaniniumcopper(II) hydrate.¹⁵

ment with several treatments of the similar CuCl_5^{3-} system.^{22, 23}

An additional band observed at high energies above 20,000 cm^{-1} is assigned to a charge-transfer band.²⁴

The table has a tabulation of the calculated E_e and E_a splittings observed for a series²² of CuCl_5^{3-} anions and the splittings observed in our compound. These quantities are directly related to the ligand field strength along the equatorial and axial positions and can be calculated using eq 1 and 2. Note

$$\Delta E_1 = 5E_e + 4E_a \quad (1)$$

$$\Delta E_2 = 10E_e + E_a$$

$$E(d_{z^2}) = 6E_e + 2E_a$$

$$E(d_{x^2-y^2}, d_{xy}) = E_e - 2E_a \quad (2)$$

$$E(d_{xz}, d_{yz}) = -4E_e + E_a$$

that the value for E_e for our compound is very similar to the values obtained for the CuCl_5^{3-} and apparently the in-plane bonding is very similar in both classes of compounds. The value for the E_a in $\text{Cu}(\text{gua})\text{Cl}_3 \cdot \text{H}_2\text{O}$ is about 20% smaller than the E_e and about 15% smaller than other E_a values; this is indicative of a somewhat weaker bonding on the axial positions in our compound, probably caused by the presence of the positively charged guaninium ion. The relative energy of the sets of d orbitals can be calculated²² using eq 2, yielding $E(d_{z^2}) = 7600 \text{ cm}^{-1}$, $E(d_{x^2-y^2}, d_{xy}) = -600 \text{ cm}^{-1}$, and $E(d_{xz}, d_{yz}) = -3100 \text{ cm}^{-1}$.

Electron Paramagnetic Resonance. The epr half-field region is shown in Figure 2. There is a distinct resonance at about 1500 G which can be assigned²⁵ to H_{min} , the minimum position of absorption in the epr spectrum of a copper(II) dimer. The observed band corresponds to the $\Delta M_s = \pm 2$ and this is indicative that the spins at the Cu(II) ions are interacting, yielding a triplet and a singlet state. A value of the zero-field splitting constant,²⁶ $|D|$, of 0.023 cm^{-1} can be calculated from this band,²⁷ using eq 3, a value of $E = 0$, and the g value obtained from the full field spectrum. Therefore, the calculated

$$D_{\text{exptl}} = \{0.75[(h\nu)^2 - 2g\beta H_{\text{min}}]\}^{1/2} \quad (3)$$

zero-field splitting constant is much smaller than $h\nu$ (0.3 cm^{-1}) and this should allow the appearance of the low- and high-field parallel and perpendicular triplet-state bands (axial symmetry and the Hamiltonian of (4) hold for this

$$H = \beta[g_z H_z S_z + g_{x,y}(H_x S_x + H_y S_y)] + DS_z^2 + (A/N)S_z I_z + (B/N)S_{x,y} I_{x,y} - 2/3D \quad (4)$$

system). However, as shown in Figure 3, the full-field spectrum of $\text{Cu}(\text{gua})\text{Cl}_3 \cdot \text{H}_2\text{O}$ is very broad and structureless. A

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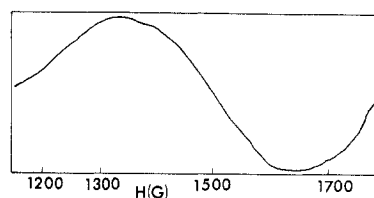


Figure 2. Half-field epr spectrum of $\text{Cu}(\text{gua})\text{Cl}_3 \cdot \text{H}_2\text{O}$; polycrystalline material, X band.

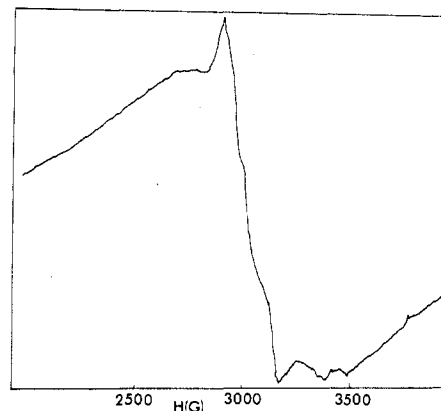


Figure 3. Full-field epr spectrum of $\text{Cu}(\text{gua})\text{Cl}_3 \cdot \text{H}_2\text{O}$; room temperature, polycrystalline material, X band.

Table I. Electronic Excitations (kK) and Equatorial and Axial Fields for Some CuL_5^{3-} Systems (10^4 kK)

Compd	ΔE_1	ΔE_2	E_e	E_a
$\text{Cu}(\text{gua})\text{Cl}_3 \cdot \text{H}_2\text{O}$	8.00	10.50	0.97	0.80
$\text{Co}(\text{NH}_3)_6\text{CuCl}_5^a$	8.40	10.10	0.96	0.91
$\text{Ru}(\text{NH}_3)_6\text{CuCl}_5^a$	8.50	10.20	0.97	0.92

^a These data from ref 18.

(g) value of about 2.18 can be obtained from the central point in the inflection. Attempts to prepare a solid solution of Zn-Cu in order to resolve the triplet-state spectrum have not been successful. A frozen solution spectrum of $\text{Cu}(\text{gua})\text{Cl}_3 \cdot \text{H}_2\text{O}$ in methyl alcohol has yielded an additional $S = 1/2$ spectrum having $g_z = 2.2$, $g_{x,y} = 2.05$, and $A_{\text{Cu}} = 150 \text{ G}$ and probably originating from decomposition products such as the broken-up monomers in solution.

It is very significant that most of the intensity of the resonance band is lost upon cooling the sample to 77°K . Apparently, the singlet state lies lowest and as the higher triplet state becomes depopulated the spectrum decays.

One more set of calculations can be done with the epr data in relation to the intermetallic distance, $R_{\text{Cu-Cu}}$. The calculated value for $R_{\text{Cu-Cu}}$ from the crystallographic data is 3.7 Å and a value of 3.6 Å is calculated^{27, 28} from eq 5, using

$$R_{\text{Cu-Cu}}^3 = \frac{0.325g_z^2(1 - 3 \cos^2 \theta)}{D_d} \quad (5)$$

$g_z = 2.20$, $\theta = 41^\circ$ (the angle between $R_{\text{Cu-Cu}}$ and the three-fold symmetry axis), and $D_d = 0.023 \text{ cm}^{-1}$ as calculated before. The agreement between the X-ray value and the epr value is excellent and somewhat fortuitous in light of the assumptions of charge localization at each copper ion and that D_{exch} is approximately equal to 0 in eq 6.^{29, 30} Also, eq 3 and 5 strictly apply to systems where the D and g tensors are

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$$D_{\text{exptl}} = D_{\text{d}} + D_{\text{exch}} \quad (6)$$

coincident. In our case these tensors do not coincide ($\theta = 41^\circ$), but apparently the error introduced is small because of the agreement between calculated and experimental R values. This same situation has been observed previously with the $\text{Na}_2\text{Cu}(\text{C}_4\text{O}_6\text{H}_2) \cdot 5\text{H}_2\text{O}$ dimer,^{27,31} where the angle $\theta = 31^\circ$ and the calculated R was also close to the X-ray experimentally determined one. It is probable from the agreement observed that the exchange contribution to the D value is small when compared to D_{d} and that therefore our assumption of $D = D_{\text{d}}$ is valid for this case. This is also indicated by the gaussian shape of the full-field epr band.

Magnetic Susceptibility. The shape of the curve of the variation in the magnetic susceptibility with temperature for $\text{Cu}(\text{gua})\text{Cl}_3 \cdot \text{H}_2\text{O}$ is the best method of determining the ground state for this system. The data are shown in Figure 4 where the \times and \circ are the experimental susceptibility and inverse susceptibility, respectively. In the temperature range 300–100°K a Curie-Weiss law³² holds with an intercept of about 100°K, indicating an antiferromagnetic interaction. The data below 100°K demonstrate this point even more clearly. There is a Neel point at about 80°K and the experimental data can be fitted well with the Van Vleck dimer,³³ eq 7.

$$\chi = \frac{Ng^2\beta^2}{3kT} (1 + 1/3 \exp(-2J/kT))^{-1} \quad (7)$$

We used a best fitting procedure previously described³⁴ and the following values for the parameters: $2J = -99 \text{ cm}^{-1}$, $g = 2.17$, $A_{\text{BF}} = 8 \times 10^{-4}$ (A_{BF} is defined as $\sum_i (\text{square of deviation of } \chi_i T_i)$).

The g value is very close to the average g value obtained by epr (internal self-consistency) and the value of $2J$ is negative, indicating that the triplet state lies about 99 cm^{-1} above the singlet ground state. The magnetic moments for this compound calculated using eq 8 are shown in Figure 5, where the

$$\mu = 2.83(\chi T)^{-1} \quad (8)$$

experimental points were calculated using eq 8 and are shown as circles and the line is the best fit output using the above values for the parameters and eq 7 and 8. As expected for a singlet ground state, the values decrease dramatically with temperature from about 1.8 BM at 300°K to about 0.5 BM at about 40°K.

Note that the magnetic susceptibility as well as the effective magnetic moment of this compound are about the normal ones at 300°K for a $S = 1/2$ case even though the ground state for the system is 0 and the interactions are quite noticeable at lower temperatures. This phenomenon should be kept in mind by investigators in this field when reporting "no interactions" from room-temperature magnetic susceptibility measurements. It will be interesting to determine if the "abnormal" electronic and magnetic properties observed for this guanine compound also occur in the nucleic acid-metal systems.

Conclusions

It has been shown from epr, electronic spectra, and magnetic susceptibility measurements that the semiquantitative diagram shown in Figure 6 holds for this system, that is, a

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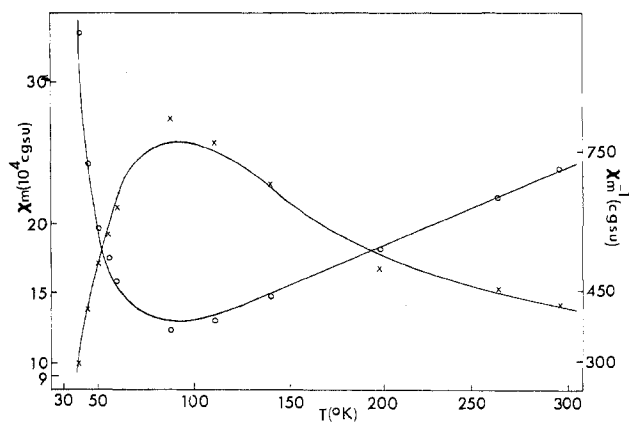


Figure 4. Experimental (\times , \circ) and theoretical (—) magnetic susceptibilities and inverse magnetic susceptibilities of $\text{Cu}(\text{gua})\text{Cl}_3 \cdot \text{H}_2\text{O}$.

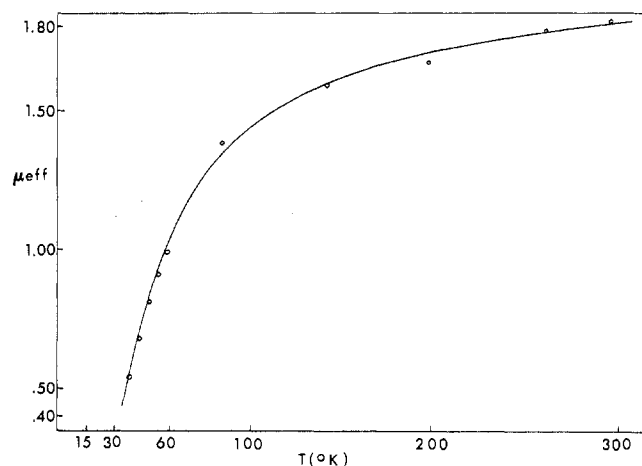


Figure 5. Experimental (\circ) and theoretical (—) effective magnetic moments for $\text{Cu}(\text{gua})\text{Cl}_3 \cdot \text{H}_2\text{O}$.

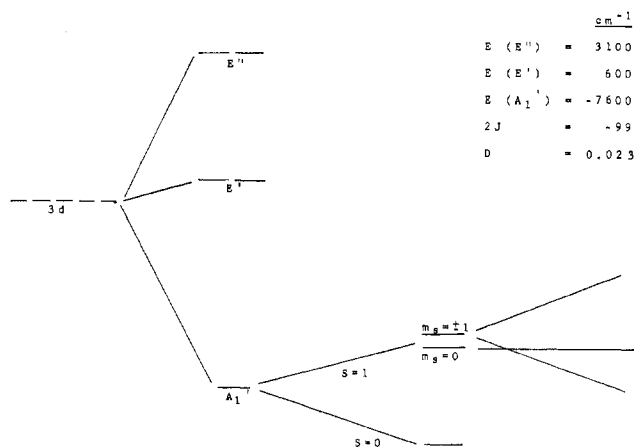


Figure 6. Energy level diagram and calculated energies for $\text{Cu}(\text{gua})\text{Cl}_3 \cdot \text{H}_2\text{O}$.

singlet ground state and a triplet excited state 99 cm^{-1} above with a zero-field splitting of 0.023 cm^{-1} . The electronic energy levels appear to be an A_1' ground state stabilized by 7600 cm^{-1} with E' and E'' about 600 and 3100 cm^{-1} higher, respectively.

Registry No. $\text{Cu}(\text{gua})\text{Cl}_3 \cdot \text{H}_2\text{O}$, 40031-94-5.

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Symmetry-Constrained Force Fields in the Prediction of Molecular Geometries of Metal Complexes. I

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The theoretical and practical aspects of symmetry-dependent strain energy refinement of the structures of metal complexes are reported. Use of this procedure reduces computation per cycle to approximately one-fifth of that required by independent refinement and in addition requires substantially less core storage. The fixing of individual cartesian atomic coordinates in both independent and symmetry-dependent refinements is discussed and in particular it is shown how a symmetry trap may be avoided. For the symmetrical facial bis(diethylenetriamine)cobalt(III) ion, results of independent and symmetry-dependent refinements constrained to two symmetry point groups are presented and compared with X-ray crystal data. Calculations on the lowest strain energy isomer of carbonatobis(trimethylenediamine)cobalt(III) are also cited.

Introduction

Recent publications¹ have reported the calculation of thermodynamic parameters and molecular geometries for metal complexes. The potential energy of a molecule with N atoms is represented by the summation

$$U_{\text{total}} = \sum U_{\text{B}} + \sum U_{\text{NB}} + \sum U_{\theta} + \sum U_{\phi}$$

where U_{B} , U_{NB} , U_{θ} , and U_{ϕ} are functions describing the potential energy of bond length deformations, nonbonded contacts, valence angle deformations, and bond torsion, respectively. The mathematical forms of these functions are adequately described, if not justified, elsewhere.² U_{total} is measured from an arbitrary zero level, which has significance only for the comparison of two stereoisomers. For an individual molecule, U_{total} represents the potential energy difference between the predicted structure and a configuration of that molecule, strainless with respect to the above four modes. Although in most instances this strainless, zero-level configuration cannot have physical reality, comparisons of potential energies with experimental data are valid for configurational isomers but specifically exclude comparisons of linkage isomers. The molecular geometry defined by minimum U_{total} and the value of U_{total} itself have been correlated with experimental data.¹

In many of the molecules studied by us, one common observation was prevalent, namely, that the molecular symmetry, intrinsic in a molecular model, was preserved almost precisely in the calculated conformation of the strained molecule. We wish to report the theoretical and practical considerations of an extension of the present refinement procedure,³ applicable to metal complexes of any point group. This extension not only allows the investigation of a metal complex constrained to its symmetric configuration(s) but also constitutes a significant reduction in computing time and memory requirements.

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Theory and Discussion

Minimization on the energy surface is implemented by curve fitting to the function U_{total} as described by Boyd.⁴ The mathematical procedure for nonrefinement of symmetry-dependent atoms is described in the Appendix.

In addition to this, we have found it necessary to incorporate a routine to fix discrete coordinates of any atom in the input list. The coordinates to be constrained are dictated by the particular symmetry conditions and disposition of atoms relative to symmetry elements. This option must be included to prevent spurious results and is discussed below.

A cycle of symmetry-dependent refinement involves modulation of the asymmetric atom positions in the force field imposed by the entire molecule. The pertinent symmetry operations are then used to reconstruct the molecule from the refined asymmetric atoms, whence the modified force field is generated and the cycle iterated. This mode is continued to convergence. The rate of convergence may depend on the size of coordinate shifts however, and a damping function should be employed to maximize this rate. However, the use of a fixed damping factor to achieve the maximum convergence rate within a particular potential energy well is unsatisfactory, since the damping is applied without reference to the size of coordinate shifts. In generating the damping factor, it has been assumed the direction of the calculated translation vector ($\Delta \mathbf{X}_i^{\alpha}$) is correct but that the magnitude is overestimated. This stems from the fact that the direction is correct at the point of fit or of extrapolation to zero magnitude and leads to a linear dependence between the corrected translation vector and the calculated one. Furthermore, it was decided that the larger elements of the translation vector should have more control over the magnitude of the estimated damping factor. In practice, calculated elements may range from 10^{-4} to 2 Å and unless stringent discrimination is required, a function dependent on the sum of the squares of the vector elements will principally reflect the larger ones. A function of the form

$$\lambda = 1 / (1 + (\text{SHAPE}) \sum_{i=1}^N \sum_{\alpha=1}^3 (\Delta X_i^{\alpha})^2)$$

is found to be adequate in reducing the possibilities of oscillation

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