Inorganica Chimica Acta, 25 (1977) 49–54
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Synthesis and Complete Electronic and Magnetic Study of a New Family of Halogen Bridged Cu(II)–Guaninium Dimer Coordination Compounds

J. F. VILLA, R. DOYLE, H. C. NELSON and J. L. RICHARDS

Department of Chemistry, H. H. Lehman College of the City University of New York, Bronx, N.Y. 10468, U.S.A.

Received February 15, 1977

A new family of Cu(II) coordination compounds has been prepared with the general stoichiometry $(CuX_3\cdot guaninium\cdot wH_2O)_2$ *where* $X = Cl$, *with* $w = 1$ *and 0, F with* $w = 1$ *and Br with* $w = 0$. *Electronic spectra were interpreted by means of a trigonal bipyramidal model for the coordination geometry around the Cu(II). The Electron Paramagnetic Resonance spectra were interpreted as originating in spin = 1 Cu(II) dimers with the* H_{MIN} *at about 1500 G and the full field bands in the 2700–3500 G region. The order of g values were* $g_\perp > g_{//}$. *The magnetic susceptibility of the compounds followed the Van Vleck dimer equation down to 12 °K and the 2J values ranged from 15 to 320* cm^{-1}. *The susceptibility for the Br compound was abnormal in that the effective moment was low and constant throughout the whole temperature range. For the chloro compound a dramatic change in the 2J value occurred upon loss of the water molecule. The IR spectra indicated that the coordination occurred at the N(9) atom in all the compounds and that the positive charge was deposited at the ring except in the fluoro compound where protonation occurred at the* NH_2 *group.*

Introduction

We have been working on the preparation and property elucidation of the coordination compounds of the nucleic acid components: the nucleotides, nucleosides and nucleic acid bases [1, 2]. These moieties afford a large number of coordination possibilities including chelation and bridging between metal ions. One particular compound, di-μ-chlorobis(dichloroguaninium)copper(II), has been shown [3, 4] to be particularly interesting since it is a strict dimer [5, 6] (see Fig. 1) bridged by chloride ions. The guanine ligand is cationic with protonation at the N atoms in the ring and the coordination is at the N(9) atom. We have now prepared a series of three new compounds that have the same formulation as the chloro dimer and present here the complete magnetic, electron paramagnetic resonance, electronic and infrared data for these compounds. These data were interpreted in order to obtain the coordination geometry around the Cu(II) ions, to determine the coordination sites and the type of magnetic interactions prevalent in these compounds. A short, preliminary report on the synthesis and IR of these compounds has appeared [7].

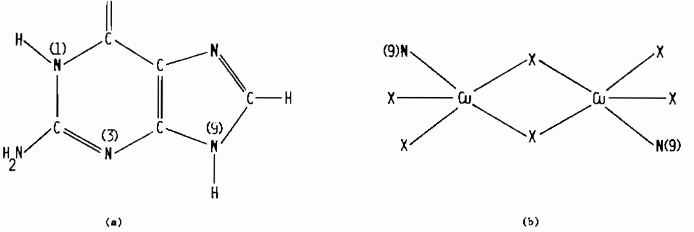

Figure 1. Schematic structures of (a) guanine and (b) the family of dimers studied here.

Experimental

Synthesis

The compounds were prepared from acidic water solutions. Plastic laboratory ware were used during the synthesis of the fluoride compound. All the compounds were stable in air except the anhydrous chloro compound which reverted to the hydrated one. All the reagents were commercially available and used without further purification and the microanalyses were done commercially by PCR, Inc., Gainesville, Florida. The correct stoichiometries were established by means of our Fortran IV fitting program LIGFIT II with a choice of six ligands (including cationic, anionic, and neutral guanine as fitting choices). The hydrated chloro compound was prepared according to the literature, had the correct stoichiometry, orange color and melting point = 240–250 °C (d).

Di-μ-chloro-bis(chloroguaninium)copper(II)

This compound was prepared by heating the hydrated compound overnight in an oven at 80 °C. The color changed to yellow from the orange color of the hydrate. Melting point = 215–240 °C (d). *Anal.* Calcd. for $CuC_5H_6N_5OCl_3$: C, 18.65; H, 1.88; N, 21.75%. Found: C, 19.06; H, 2.02; N, 22.28%.

Di-μ-bromo-bis(bromoguaninium)copper(II)

Guanine (3.01 g) was added to a solution of 13.0 g of $CuBr_2$ in 100 ml of concentrated HBr yielding a very dark, almost black solution. The solution was heated to 100 °C allowing about half of the solution to evaporate. Upon cooling to room temperature, a black, crystalline solid formed, was filtered and dried at 90 °C for an hour. Melting point = 244–260 °C (d). *Anal.* Calcd. for $CuC_5H_6N_5Br_3$: C, 13.18; H, 1.33; N, 15.38%. Found: C, 13.43; H, 1.67; N, 16.03%.

Di-μ-fluoro-bis(fluoroguaninium)copper(II) Dihydrate

A mixture of 10.9 g of $CuF_2 \cdot 2H_2O$ and 3.01 g guanine was prepared in 200 ml of 0.2 *M* HF and strongly stirred for four days. The color changed slowly from blue to green. The green solid was filtered, washed with water and dried at 90 °C for three hours. Melting point = 200–240 °C (d). *Anal.* Calcd. for $CuC_5H_8N_5O_2F_3$: C, 20.66; H, 2.77; N, 24.09%. Found: C, 20.40; H, 3.39; N, 23.65%.

Magnetic Studies

The magnetic susceptibility of all the compounds reported here were obtained in a Faraday setup in the temperature range 12 °K to room temperature at 7,000 G. A Cahn balance model G-2, Alfa current regulated power supply and magnet (Faraday tapered pole pieces) and an Air Products mechanical refrigerator and Faraday shroud to vary the temperature were used. The temperature was measured with a chromel–iron-doped gold thermocouple and a hydrogen bulb thermometer.

Spectroscopic Studies

The EPR spectra were obtained in a Varian Associates HFE-12 spectrometer at the X-band. Scans were to 20,000 G and at room temperature and 77 °K. The IR spectra were obtained in a Perkin Elmer IR-21, as KBr pellets in the 4,000–600 cm^{-1} range. The UV–VIS–near IR spectra were obtained in a Beckman DK-2A spectrophotometer as Nujol mulls on filter paper in the 200–2,000 mμ range.

Results and Discussion

The principal bands in the IR spectra of these compounds were assigned by comparison of the spectrum of the free ligands to the ligands in the coordination compounds and also by comparison to previous isotopic substitution work present in the literature [8]. The areas of interest are the $\nu C(6)O$ present at about 1710 cm^{-1}; and the $\delta N(1)H$, $\delta N(3)H$, $\delta N(7)H$ and $\delta N(9)H$ at about 1510, 1500, 1420 and 1415 cm^{-1} respectively.

The positions of absorption for these five bands in the free guanine, chloro hydrate, chloro anhydrous, fluoro and bromo are, respectively (in cm^{-1}): 1710, 1510, –, – and 1415; 1705, 1520, 1500, 1430, –; 1725, 1520, 1500, 1420, –; 1705, 1510, –, 1420, –; and 1720, 1535, 1500, 1430, –.

Firstly it should be noticed that the $\delta N(9)H$ observed in the free ligand is not present in any of the compounds studied here, indicating coordination via the N(9) hydrated chloro compound. Secondly, also common to all the compounds is non-involvement by the C(6)O since the $\nu C(6)O$ does not change from free to coordinated ligand throughout the series. Thirdly, all the coordination compounds except the fluoro compound exhibit $\delta N(3)H$ as well as N(7)H, indicating that all the non-coordinating N atoms in the ring are protonated (including the originally protonated N(1)). Finally, the fluoro compound exhibits additional bands at 1600 and 1540 cm^{-1} which can be assigned to δNH_3^+, indicating that the protonation in this compound is at the NH_2 group. It is apparent, then, that the coordination in all of these compounds is solely via the N(9) atom and the protonation is at the remaining ring nitrogen, except in the fluoro compound.

The EPR spectra of these compounds are very informative. The spectra of all the compounds (except the Br) exhibit an H_{MIN}, the minimum position of absorption in the EPR spectrum of spin coupled Cu(II) dimers. The H_{MIN} bands including one of the Cl compound as a solid solution in the preparation mother liquor, are shown in Fig. 2 and the resonance positions are given in Table I. It can be seen that they are in the range for H_{MIN} and that if the hyperfine interactions are resolved, such as the chloride compound in solid solution, they have a magnitude of about 75 G or about half the normal value. This is to be expected from a dimeric electronic system interacting simultaneously with the two Cu nuclei each with a nuclear spin of 3/2. From the resonance positions of H_{MIN} and equation I, the Zero Field Splitting parameter D can be calculated [9]. The values are given in Table I.

$$D_{exptl} = \{0.75\,[(h\nu)^2 - 2g\beta H_{MIN}]\}^{1/2} \qquad \text{(I)}$$

The full field spectra can also be interpreted as originating in triplet state species with axial symmetry.

TABLE I. Electronic Spectra Data and Electronic Energy Levels for the Cu Guaninium$^+$ X_3 Compounds.

	E_1^a	E_2	E_e	E_a	$-E_{z^2}$	E′	E″	ΔE (A_1 − E′)
Cu Gua$^+$ Br_3	6250	9620	0.92	0.42	6480	320	2920	6800
Cu Gua$^+$ $Cl_3 \cdot H_2O$	8000	11400	1.07	0.66	7740	250	3620	7990
Cu Gua$^+$ Cl_3	8890	11100	1.02	0.95	8020	880	3130	8900
Cu Gua$^+$ $F_3 \cdot H_2O$	12100	14200	1.29	1.41	10560	1530	3750	12090

^{a}All energies in cm^{-1}.

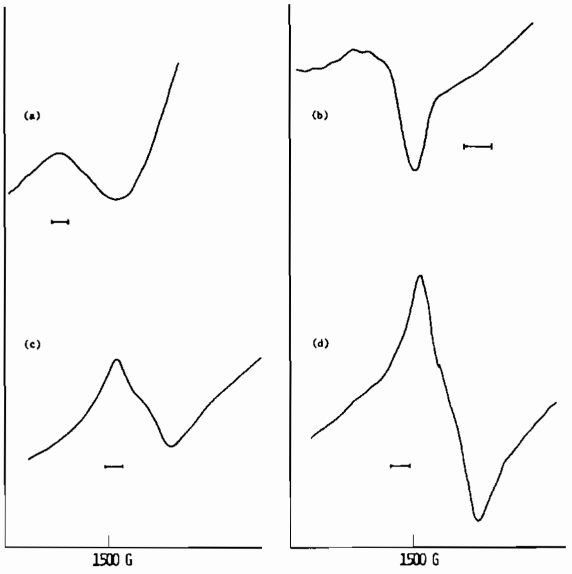

Figure 2. H_{MIN} for (a) Cl (hyd); (b) Cl in frozen solution, (c) Cl (anh) and (d) F dimers. Microwave frequencies are: (a) 9.193, (b) 9.250, (c) 9.301 and (d) 9.305.

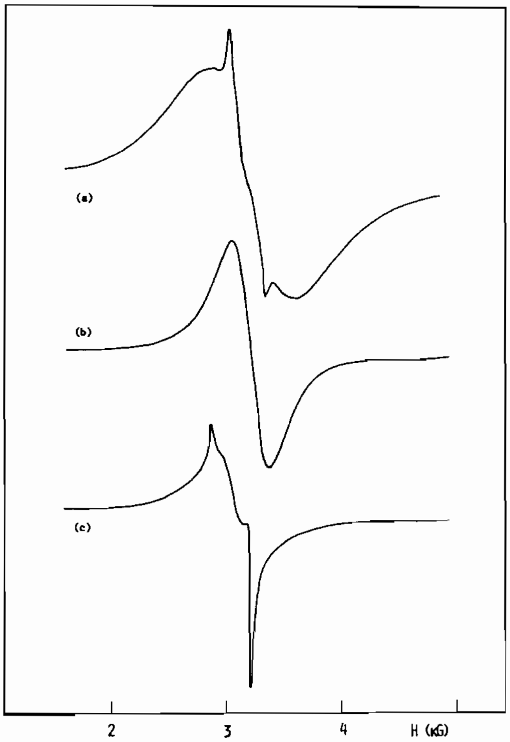

Figure 3. Full field EPR spectra of (a) Cl (hyd), (b) Cl (anh) and (c) F. Microwave frequencies are: (a) 9.289, (b) 9.290 and (c) 9.291.

These spectra (except the Br compound which does not resonate) are shown in Figure 3. The low and high field perpendicular bands are assigned in the figure and appear almost as one broad band. D values can be approximated using these full field assignments assuming that the band-width is due to the two extreme perpendicular bands, low and high field, and following the usual treatment. They are given in Table I. They agree well with the D values calculated from the H_{MIN} band and are of the right order of magnitude for the coalesced type of full field spectra observed. The spectrum of the fluoro compound is somewhat obscured by the superposition of a small amount of monomer impurity (see the magnetic susceptibility fit).

The calculated g values are also given in Table I and reflect a $g_\perp > g_{//}$ value for all of these compounds indicating that the d_{z^2} is the orbital ground state for the whole family. The bromide compound does not have an EPR spectrum. This is compatible with strong spin–spin interactions, with the ground state a spin singlet, the triplet excited state at high energies (compared to kT), and low population of the triplet state. This is corroborated by the magnetic susceptibility work. Also, the D value must be greater than the spectrometer frequency, $D > 0.3$ cm^{-1}.

The magnetic susceptibilities for the anhydrous chloro and fluoro compounds are given in Figures 4 and 5. The experimental data was fitted by means of an iterative Fortran IV program to the Van Vleck dimer [10] equation II and the parameters g and 2J

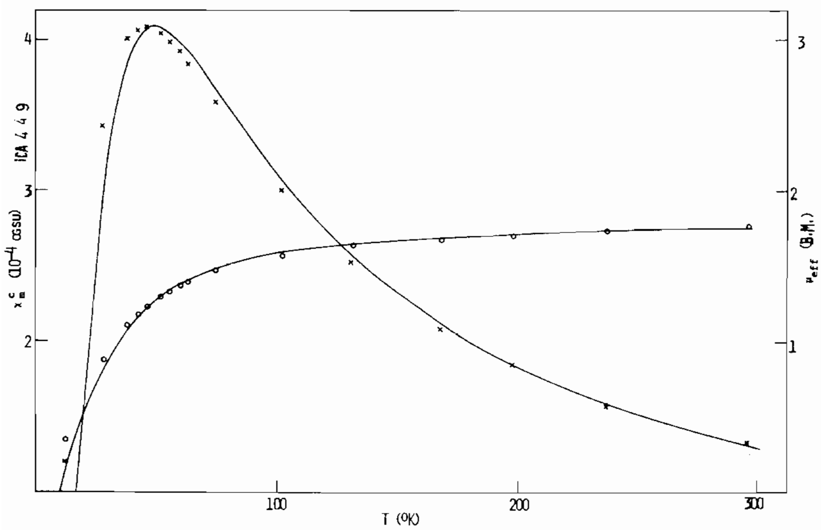

Figure 4. Experimental (X) and theoretical (–) magnetic susceptibility; and experimental (o) and theoretical (–) magnetic moment for the chloro (anh) dimer.

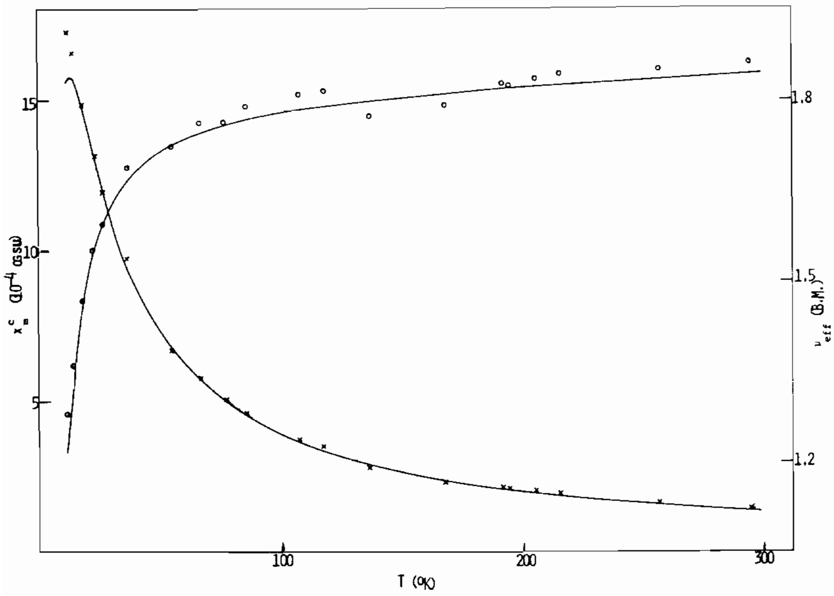

Figure 5. Experimental (X) and theoretical (–) magnetic susceptibility; and experimental (o) and theoretical (–) magnetic moment for the fluoro dimer.

obtained from the "best fit" output. These values are given in Table I and are indicative of spin–spin interactions between Cu(II) species in a strict dimeric form since equation II applies only to dimers. It can be seen that the theoretical fits are excellent (sums of the squares of the deviations were 5 X 10^{-4} and 1 X 10^{-3}, respectively) and that the g values obtained from the best fits are very similar to the values obtained by EPR. The continued increase in susceptibility of the fluoro compound at temperatures below 14 °K reflect a small amount of paramagnetic impurity. The values for the effective magnetic moment decrease with temperature indicating that the coupling in these compounds is antiferromagnetic in nature. The negative sign of 2J corroborates this and points to a singlet ground state with the triplet state at 55 cm^{-1} and 15 cm^{-1} for the chloro anhydrous and fluoro compounds, respectively.

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

It is very interesting to compare the value of 2J between the two chlorides, the anhydrous one

TABLE II. EPR and Magnetic Parameters for the Cu Guaninium$^+$ X_3 Compounds. a) From full field EPR spectrum; b) from magnetic susceptibility best fit; c) from H_{MIN}; d) from full field bands; e) from references 3 and 4.

	g_{MIN}	$g_{\perp}^{a}$	$g^{b}_{best\ fit}$	D^{c}_{MIN} (cm^{-1})	D^{d} (cm^{-1})	2J (cm^{-1})
$CuGua^+Br_3$	–	–	~2.10	>3000	–	~320
$CuGua^+Cl_3 \cdot H_2O$	4.38 (4.22)^f	2.07	2.12^e	800	720	85^e
$CuGua^+Cl_3$	4.26	2.10	2.05	500	330	55
$CuGua^+F_3 \cdot H_2O$	4.20	2.14	2.13	180	290	15

^{f}From the solid solution H_{MIN}.

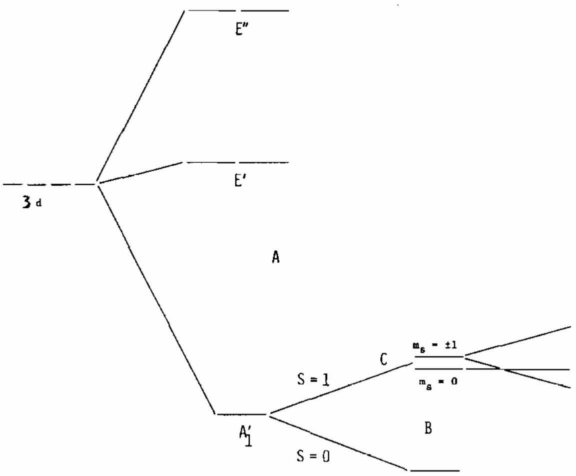

Figure 6. Complete energy level scheme for the dimers studied here. Energies A, B and C are given in Tables I and II.

reported here and the previously reported hydrate [1, 2], see Table I. A dramatic decrease by about 40% occurs upon loss of the water molecule. It should be emphasized that this water molecule is not coordinated to Cu(II) but is only trapped in the crystal lattice. Apparently, the loss of the water reflects itself in a change in the Cu–Cl–Cu bond angle decreasing the delocalization between the two Cu(II) ions.

The temperature dependence of the susceptibility for the bromo compound is extraordinary and is given here in the form of temperature (°K), corrected molar susceptibility (X 10^6 cgsu) and effective magnetic moments (B.M.): 297, 774, 1.36; 257, 875, 1.35; 244, 930, 1.35; 223, 1020, 1.35; 184, 1202, 1.34; 163, 1378, 1.35; 140, 1585, 1.34; 120, 1922, 1.36; 97, 2411, 1.37; 73, 3227, 1.38; and 49, 4703, 1.36. As can be seen, the magnetic moment is low at room temperature and remains constant within ±0.02 units down to very low temperatures. Apparently, as the temperature decreases, there are slight changes in the lattice which change the Cu–Br–Cu angle and delocalization properties of the bridging ligand to just compensate for the expected decrease in the moment. A value for 2J of –320 cm^{-1} is approximated (with a g value of 2.10 similar to the other compounds) using the room temperature susceptibility. This sets up the series of increasing 2J values as follows: F < Cl(anh) < Cl < Br which is what would be expected from a consideration of the amount of overlap between the bridging halogen ion and the Cu(II) ions.

The energy of absorption in the electronic spectrum for these compounds is given in Table II. Two bands appear for each compound in the near IR region. These bands can be interpreted as originating in a trigonal bipyramidal [11] Cu(II) ion with energies given by equations III:

$$E_1 = 5E_e + 4E_a$$

$$E_2 = 10E_e + E_a$$

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

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

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

Here E_1 and E_2 represent the two observed transitions, E_e and E_a represent the relative equatorial and axial ligand fields from which the relative energies of the d orbitals can be obtained. All the data is given in Table II. It can be noticed that the values for both E_e and E_a increase from the bromo to the chloro and fluoro ligand. This can be rationalized in terms of a size decrease from bromo to chloro to fluoro which produces a larger electrostatic ligand field as the size of the atom decreased. That is, the small and hard fluoro atom is able to approach and disturb the Cu(II) ion more than the much larger bromo atom. It can also be noticed that, as expected, the relative stabilization of the A_1 state and destabilization of the E' and E'' states follow the same pattern according to the size of the ligands. This is clearly shown in the last column of Table II where the energy differences between A and E' are given, again ranging from 6800 cm^{-1} for the bromo to 12090 for the fluoro compound.

Three new members of the bis-X(diXguaninium)-copper(II) series, where X = Cl, Br and F, have been prepared. The coordination site of the purine base was N(9) and constant throughout the series and protonation occurred at all the heterocyclic nitrogen atoms except the fluoro compound with protonation at the exocyclic amino group. The coordination geometry was established as trigonal bipyramidal.

All the relative energies schematically represented in the diagram in Fig. 6 were also determined. The electronic energies, A, determined from the electronic spectra are in the expected order for the small fluoro atom compared to the larger chloro and bromo ligands. The coupling energies between the two copper(II) ions in each dimer, B, decreased from the Br bridged dimer, indicating that the coupling mechanism is via superdelocalization through the halogen group. Finally, D, the Zero Field Splitting energy or separation between the ±1 and 0 M_s levels, C, decreased from Br to F indicating a larger distortion in the Br compound, which is also in agreement with the ligand field treatment.

Finally, it was observed that the simple loss of a water of hydration can change the magnetic properties of the compound dramatically. This should be kept in mind when comparing the magnetic properties of coupled compounds prepared at different times using slightly different preparative or storing conditions which might be conducive to loss or pick up of water molecules.

Acknowledgments

We are pleased to acknowledge financial support from a G. N. Shuster Fellowship and from a Petroleum Research Fund Grant administered by the American Chemical Society. We also thank Ms. Ngarling Khoe for help with the computer programs.

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