reported for Mn^{2+}. Again, either the resonance is attributable to Mn^{2+}impurity with absolutely no Mn^{3+}resonance or it is of Mn^{3+} which happens to be the same as that for the Mn^{2+}because of the isotropic nature of the Mn^{3+}caused by pseudorotion,a most disconserting situation, indeed. It is surprising that pseudorotation should be operative at liquid nitrogen temperatures in the light of other published data for Jahn-Teller prone systems invest i gated at these temperatures.

Should the EPR spectra obtained be entirely from the Mn^{2+}impurity, one could suggest two possible explanations for the absence of Mn^{3+}resonance(s). Either there is distortion leading to such a large zero-field splitting that no resonance is seen, or the spin-lattice relaxation T_1 is unsuitable for the obtaining of EPR spectre. these questions must remain to be answered by a exhaustive investigation.

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temperature, the resonances at low field disappear. Previous work on Mn^{3+} in Al_2O_3 indicated that the hyperfine structure for Mn^{3+} could only be resolved below about 2.5K.[8]

To minimize interference between neighboring paramagnetic units diluts solution and solids were also studied. The EPR spectra of Mn^{3+}-doped $[Al(urea)_6](ClO_4)_3$ at room temperature and liquid nitrogen temperature are givon in Figures 2 and 3, respectively. The room temperature spectrum contains only one sharp peak at g = 1.98, but liquid nitrogen temperatur this peak splits into at least two resenances which we assign as $g = 1.99$ and $g = 1.95$. No hyperfine structure is observed for Mn^{3+}-doped $[Al(urea)_6](ClO_4)_3$ either at room temperature or liquid nitrogen temperature- These spectra were obtained not only with a 1000-gauss sweep, but with a 5000-gauss sweep as well to ensure that no resonance had been missed. The several weak resonances lying downfield from the $g \cong 2$ resonance were shown to be impurities by dilution of the Mn^{3+}-doped samples- Indeed, these reso nances attributed to sample impurities are observed for the Mn-free $[Al(urea)_6](ClO_4)_3$.

In an attempt to support the assignment ot the resonances observed at $g_{\|} = 1.99$ and at $g \cong 1.95$ to Mn^{3+} rather than to attribute it to small amounts of Mn^{2+} impurity from some decompositon of the Mn^{3+} the EPR spectrum of $[Al(urea)_6](ClO_4)_3$ doped with $Mn(ClO_4)_2 \cdot 6H_2O$ was run at liquid nitrogen temperature. In the region of interest, the two spectra (one conteining only Mn^{2+} and the other thought to contain only Mn^{3+}) were indistinguishable. There is no doubt that the sample doped with the Mn^{3+} compound contains predominantly Mn^{3} The sample has a pronounced pink color even when the Mn^{3} to Al^{3+} ratio is 15:1000. A sample of pure $Mn(ClO_4)_2$ is scarcely colored because of the spin-forbiddenness of the optical transitions. Also the Mn^{3} and MnO_2 when placed in water. Should the EPR spectra be those of Mn^{2}, the Mn^{2} impurity must be present in trace amouse.

The EPR spectrum of $[Mn(urea)_6](ClO_4)_3$ in absolute ethanol glass at liquid nitrogen temperature is identical with that obtained in urss saturated $HClO_4$ (60%) (in which it is improbable that reduction of Mn^{3+} will take place). These spectra contain six prominent lines with forbidden transition lying midway between them (Figure 4) ($g = 2.00$, and $A \cong 92$), essentially identical to that

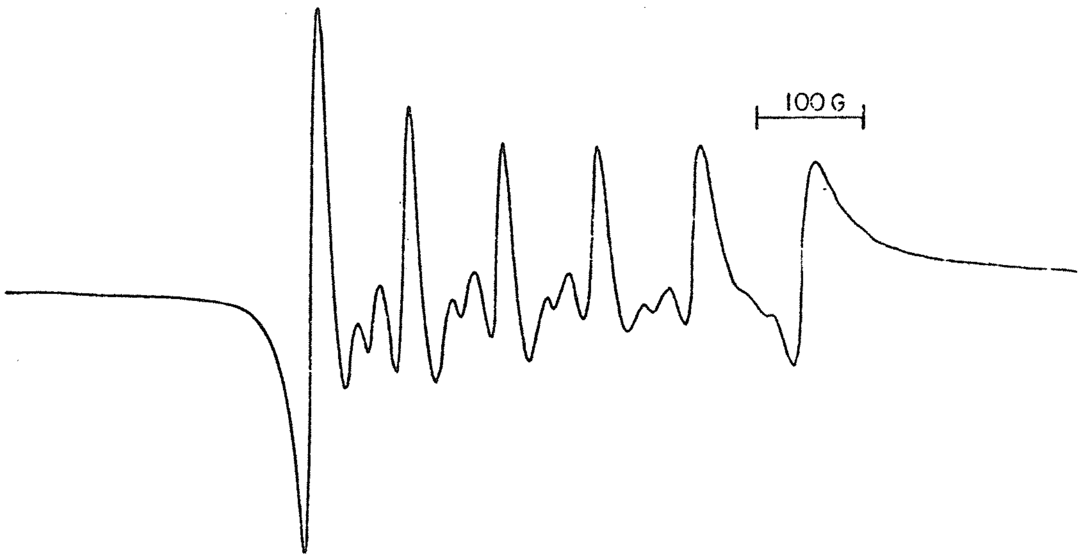

Figure 4. EPR spectrum of $[Mn(urea)_6](ClO_4)_3$ in perchloric acid (60%) saturated with urea at liquid nitrogen temperature.

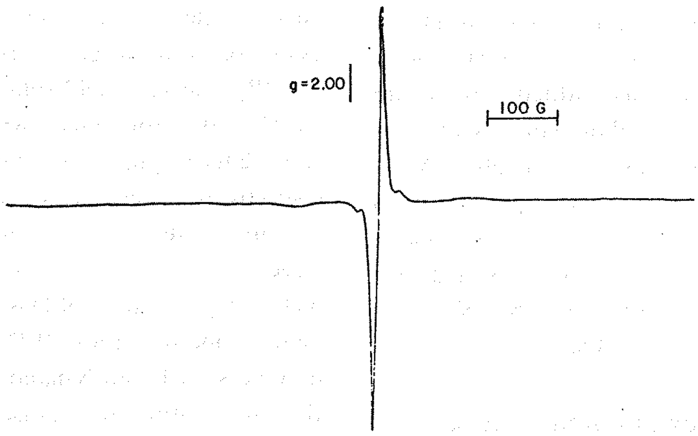

Figure 2. EPR Spectrum of microcrystalline manganese (III)-doped $[Al(urea)_6](ClO_4)_6$ at room temperature.

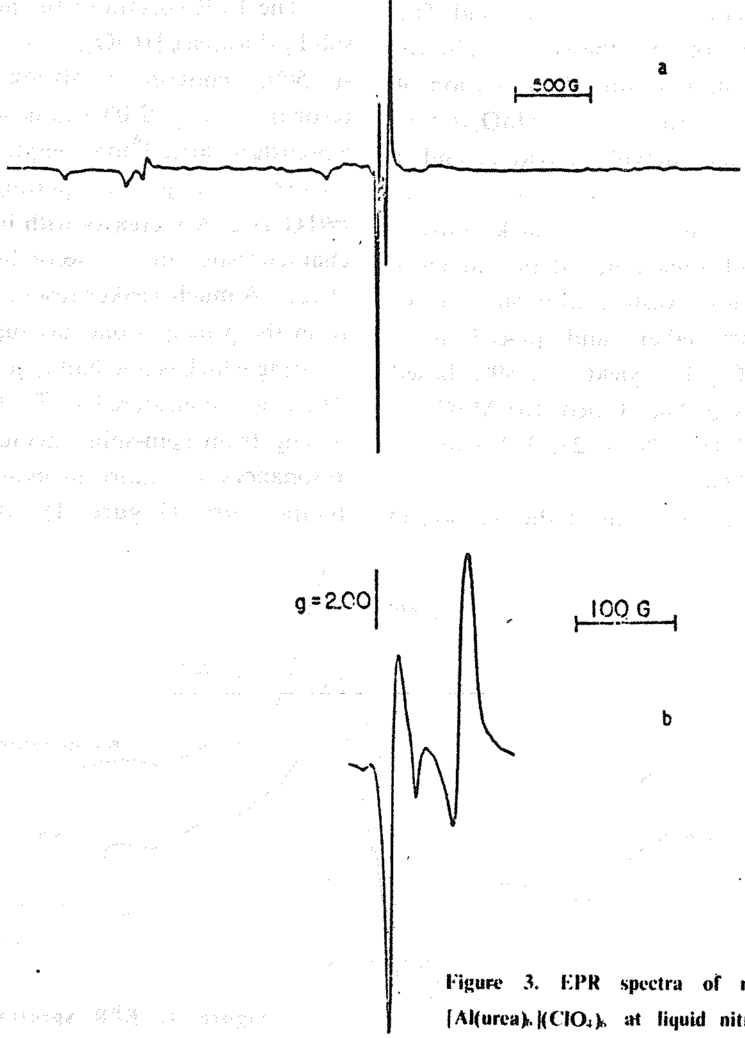

Figure 3. EPR spectra of manganese (III)-doped $[Al(urea)_6](ClO_4)_6$ at liquid nitrogen temperature (a) 2500 and (b) ±500 Scan range.

(8.0 g, 0.033 mol) was dissolved in the minimum amount of water (total solutionvolume, 20 ml). to this solution, perchloric acid (140 ml of 60% acid) saturated with urea was added A white microcrystalline solid formedimmediately and was separated by filtration, washed with 50% (V/V) absolute ethanol-dry ether and placed in a dessicator over $CaCl_2$. The yield was 92% based upon the $AlCl_3.6H_2O$ used. Anal. Calcd. for $AlC_6N_{12}H_{24}Cl_3O_{18}$: C, 10.51; H, 3.53; N, 24.51, Found: C.10.60; H, 3.40; N.24.60.

Preparation of Hexaureamanganese (III) Perchlorate

Powdered manganese (10.0 g, 0.182 mol) was added to 400 ml of refluxing glecial acetic acid. The manganese slowly dissolvedin the stirred solution over about 4h. To the hot, stirred suspension of manganese (II) acetate was added $KMnO_4$ (6.5 g, 0.041 mol). After 25 min, perchloric acid (250 ml of 60% acid) saturated with urea was added to the warm, dark red solution. A dark purple microcrystalline solid fromed immediately and was separated by filtration, washed with 50% (V/V) absolute ethanol-dry ether, and placed in a dessicator over $CaCl_2$ The yield was 80% based upon the $KMnO_4$used. Anal Calcd. for $MnC_6N_{12}H_{24}Cl_3O_{18}$: C, 10.10; H, 3.39; N, 23.55. Found: C, 9.67; H, 3.66; N, 22.66.

An octahedral perturation of the free ion ^5D term gives a ^5E ground term. This term should be further splitbyaJahn-Teller effect manifested as an axial elongation to give a $^5B_{1g}$ ground term.[7] From the ^5B1g, via zero-field splitting, thereare obtained the $M_s = 0$ ground term with the excited $M_s = \pm1$ and ±2 term lying above it by an energy D and 3D, respectively. There are then four $\Delta M_s = \pm1$ EPR transitions allowed between these levels if D is not large. If D is very small or zero, the four transitions will be degenerate; or if D is rather large, there may be only one transition. If D is large, no transitions may be seen by an X-band spectrometer. Because the only isotope of manganese is ^{55}Mn having a nuclear spin of 5/2,each of the spectral lines seen should be split into six $(2I + 1)$ components.[1 — 6]

The EPR spectra of the pure microcrystalline solid $[Mn(urea)_6](ClO_4)_3$ at room temperature and at 50^0C contain a strong and very broad resonance with g=2.00,a value which is expected for a pseudorotated d^4 ion complex. The resonance has the expected hyperfine splitting for I=5/2 with A =91G That A increases with increasng field (H) is characteristic of a second-order perturbation effect.[2] A much weaker resonance lying downfield from the principal one has superimosed hyperfine splitting which is one-half that of the g=2 resonance These are considered to be forbidden transition arising from spin-spin interaction. The forbidden resonances are more pronounced at the higher temperature (Figure 1). At liquid nitrogen

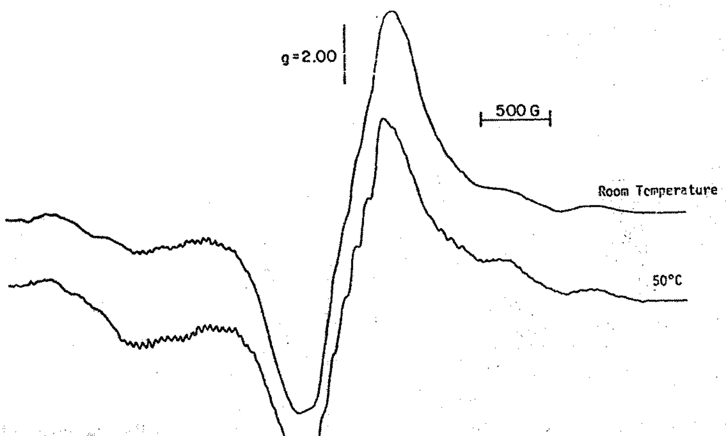

Figure 1. EPR spectra of microcrystalline $[Mn(urea)_6](ClO_4)_3$.

Electron Paramagnetic Resonance of the Hexaureamanganese (III) Perchlorate

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ABSTRACT

EPR spectra of hexaureamanganese (III) perchlorate were obtained both at room temperature and at liquid nitrogen temperature on microcrystalline of $[Mn(urea)_6](ClO_4)_3$ and manganese (III) - doped $[Al(urea)_6](ClO_4)_3$, on glasses of $[Mn(urea)_6](ClO_4)_3$ in C_2H_5OH(obsolute) and in perchloric acid (60%) saturated with urea. The room temperature spectrum contains only one sharp peak at g=1.98, but at liquid nitrogen temperature. this peak splits into at least two resonances which we assign as $g_{11}=1.99$ and $g_1=1.95$. No hyperfine structure is observed for $Mn^3 \pm$ doped $[Al(urea)_6](ClO_4)_3$ either at room temperature or liquid nitrogen temperature.

Electron Paramagnetic Resonance (EPR), Electron Spin Resonance (ESR), or Electron Magnetic Resonance is a powerful tool that can give a wealth of information about the electronic, magnetic, and the structure or environment of a paramagnetic species. EPR is a branch of absorption spectroscopy. When a paramagnetic specimen is placed in a permanent magetic field and subjected to radiation of microwave frequency, microwave power is absorbed by the specimen at a particular frequency. As a general rule, to minimize interference between neighboring paramagnetic units, dilute solutions, solid liquid, are studied. It is also better to work at low temperature, where linebroadening effects are reduced. [1—6].

EPR spectra were obtained both at room temperature at liquid nitrogen temperature on microcrystalline of $[Mn(urea)_6](ClO_4)_3$ and manganese (III)-doped $[Al(urea)_6](ClO_4)_3$, on glasses of $[Mn(urea)_6](ClO_4)_3$ in C_2H_5OH (absolute) and in perchloric acid (60%) saturated with urea. All EPR spectra were recorded by means of a Varian E-3 spectrometer at a microwave power of 8.0 mW, a microwave frequency of 9.10±0.1 GHz, and a modulation amplitude of 1 to 5 G.

Preparation of Hexaureaalumium Perchlorate

Hydrated aluminum chloride, $AlCl_3.6H_2O$,