reported for Mn\textsuperscript{2+}. Again, either the resonance is attributable to Mn\textsuperscript{2+} impurity with absolutely no Mn\textsuperscript{3+} resonance or it is of Mn\textsuperscript{3+} which happens to be the same as that for the Mn\textsuperscript{2+} because of the isotropic nature of the Mn\textsuperscript{3+} caused by pseudorotation, a most disconcerting 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 investigated at these temperatures.

Should the EPR spectra obtained be entirely from the Mn\textsuperscript{3+} impurity, one could suggest two possible explanations for the absence of Mn\textsuperscript{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.

### Reference

temperature, the resonances at low field disappear. Previous work on Mn$^{3+}$ in Al$_2$O$_3$ indicated that the hyperfine structure for Mn$^{1+}$ could only be resolved below about 2.5 K.\textsuperscript{8}

To minimize interference between neighboring paramagnetic units dilute solution and solids were also studied. The EPR spectra of Mn$^{1+}$-doped [Al(urea)$_n$(ClO$_4$)$_2$] at room temperature and liquid nitrogen temperature are given in Figures 2 and 3, respectively. The room temperature spectrum contains only one sharp peak at $g = 1.98$, but liquid nitrogen temperature this peak splits into at least two resonances which we assign as $g = 1.99$ and $g = 1.95$. No hyperfine structure is observed for Mn$^{3+}$-doped [Al(urea)$_n$(ClO$_4$)$_2$] 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 $g = 2.2$ resonance were shown to be impurities by dilution of the Mn$^{1+}$-doped samples. Indeed, these resonances attributed to sample impurities are observed for the Mn-free [Al(urea)$_n$(ClO$_4$)$_2$].

In an attempt to support the assignment of the resonances observed at $g // = 1.99$ and at $g ^ \bot = 1.95$ to Mn$^{3+}$ rather than to attribute it to small amounts of Mn$^{2+}$ impurities from some decomposition of the Mn$^{3+}$, the EPR spectrum of [Al(urea)$_n$(ClO$_4$)$_2$] doped with Mn(ClO$_4$)$_2$, 6H$_2$O was run at liquid nitrogen temperature. In the region of interest, the two spectra (one containing only Mn$^{3+}$ and the other thought to contain only Mn$^{1+}$) were indistinguishable. There is no doubt that the sample doped with the Mn$^{1+}$ compound contains predominantly Mn$^{1+}$. 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 Mn$^{2+}$ when placed in water. Should the EPR spectra be those of Mn$^{3+}$, the Mn$^{2+}$ impurity must be present in trace amount.

The EPR spectrum of [Mn(urea)$_n$(ClO$_4$)$_2$] 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 $\Delta g \approx 92$), essentially identical to that

![Figure 4. EPR spectrum of [Mn(urea)$_n$(ClO$_4$)$_2$] in perchloric acid (60\%) saturated with urea at liquid nitrogen temperature.](image-url)
Figure 2. EPR Spectrum of microcrystalline manganese (III)-doped \([\text{Al(urea)}_2\text{ClO}_4]_2\) at room temperature.

Figure 3. EPR spectra of manganese (III)-doped \([\text{Al(urea)}_2\text{ClO}_4]_2\) 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 solution volume, 20 ml). to this solution, perchloric acid (140 ml of 60% acid) saturated with urea was added A white microcrystalline solid formed immediately and was separated by filtration, washed with 50% (V/V) absolute ethanol-dry ether and placed in a dessicator over CaCl₂. The yield was 92% based upon the AlCl₃,6H₂O used. Anal. Calcld. for AlC₈N₁₂H₁₂Cl₃O₁₄: C, 10.51; H, 3.53; N, 24.51. Found: C10.60; 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 glacial acetic acid. The manganese slowly dissolved in the stirred solution over about 4 h. To the hot, stirred suspension of manganese (II) acetate was added KMnO₄ (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 formed immediately and was separated by filtration, washed with 50% (V/V) absolute ethanol-dry ether, and placed in a dessicator over CaCl₂. The yield was 80% based upon the KMnO₄ used. Anal. Calcld. for MnC₅N₁₂H₂₄Cl₃O₁₄: C, 10.10; H, 3.39; N, 23.55. Found: C, 9.67; H, 3.66; N, 22.66.

An octahedral perturbation of the free ion ³D term gives a ³E ground term. This term should be further split by a Jahn-Teller effect manifested as an axial elongation to give a ³B₁g ground term. From the ³B₁g, via zero-field splitting, there are obtained the Ms = 0 ground term with the excited Ms = ±1 and ±2 term lying above it by an energy D and 3D, respectively. There are then four AMs = ±1 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 ⁵⁵Mn having a nuclear spin of 5/2, each of the spectral lines seen should be split into six (2I + 1) components.

The EPR spectra of the pure microcrystalline solid [Mn(urea)]₃ClO₄ at room temperature and at 50°C contain a strong and very broad resonance with g = 2.00, a value which is expected for a pseudorotated d⁴ ion complex. The resonance has the expected hyperfine splitting for I = 5/2 with A = 91G. That A increases with increasing field (H) is characteristic of a second-order perturbation effect. 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
**Electron Paramagnetic Resonance of the Hexaureamanganese (III) Perchlorate**

Hossein Aghabozorg and R.C. Stoufer

Chem. Dept. Univ. of Teacher Education - IRAN
Chem. Dept. Univ of Florida, U.S.A

**ABSTRACT**

EPR spectra of hexaureamanganese (III) perchlorate were obtained both at room temperature and at liquid nitrogen temperature on microcrystalline of [Mn(urea)₆](ClO₄)₂ and manganese (III) - doped [Al(urea)₆](ClO₄)₂ on glasses of [Mn(urea)₆](ClO₄)₂ in C₆H₅OH (absolute) 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 g₁ = 1.99 and g₂ = 1.95. No hyperfine structure is observed for Mn²⁺ doped [Al(urea)₆](ClO₄)₂ 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 magnetic 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](ClO₄)₂ and manganese (III)-doped [Al(urea)₆](ClO₄)₂ on glasses of [Mn(urea)₆](ClO₄)₂ in C₆H₅OH (absolute) and in perchloric acid (60%) saturated with urea. All EPR spectra were recorded by means of a Varian E-3 spectrometer at 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 Hexaurea aluminium Perchlorate**

Hydrated aluminium chloride, AlCl₃·6H₂O.