An ESR and Differential Scanning Calorimetric Study of Co(NH₃)₆(Cd:Cu)Cl₅

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There has been considerable interest in the spectra of the MCl_5^{3-} ions ($M = Cu^{2+}$ and Cd^{2+}) because of the regular geometry they exhibit ($32; D_{3h}$) when crystallized in the form of the $Cr(NH_3)_6^{3+}$ of the $Co(NH_3)_6^{3+}$ salt [1, 2]. Because of this crystallographically required point group symmetry it is an ideal material for a variety of spectroscopic studies and it is, therefore, not surprising that infrared [2], optical studies [3] and theoretical calculations [4–6] have been made on these pentachlorometallate systems. Finally, measurements of the bulk magnetic susceptibility down to 2.4 °K have also been carried out [7] and the results appeared normal for a simple paramagnet. A detailed study of the ers spectrum of the Cu^{2+} salt diluted in the isomorphous [2, 8] Cd^{2+} derivative seemed desirable inasmuch as the measurements reported earlier by Mori, *et al.* [1] were carried out in an undiluted sample which generally obscures results due to dipolar interaction broadening.

Experimental

The cobalt hexaamine compounds were prepared as described earlier [2, 8]. Crystalline samples of the copper-doped cadmium salt were prepared [8] in a U-tube partially filled with silica gel. In one arm was placed a solution of $Co(NH_3)_6Cl_3$ and the other arm was filled with a $CuCl_2$–$CdCl_2$ solution in which the

ratio of $Cu^{2+}:Cd^{2+}$ was 21:1. This is necessary because of the high solubility of the Cu^{2+} salt and of the very high insolubility of the Cd^{2+} derivative. When the ratio is 1:1, for example, no esr spectrum of Cu^{2+} is detectable in the resulting crystals. The small golden-yellow single crystals were washed with dilute HCl in order to remove any surface $CuCl_2$ which may have deposited, if any. All subsequent measurements were made in powdered samples from these crystals since none of them were large enough for the detection of single crystal esr spectra. A detailed description of the characteristics of crystals obtained by this methods has been given before [2, 8]. The calorimetric measurements were made in preliminary runs with powdered single crystals and with bulk material obtained during the course of our synthetic work [2]. Since the results were identical the final calorimetric measurements being reported here were made with bulk material. Esr measurements were made with a standard Varian V4502 spectrometer and the differential scanning calorimetric measurements were made with a Perkin-Elmer DSC-2 instrument using techniques described in detail by O'Neill [9]. The temperature measurements were calibrated by melting n-decane ($T_m = 243.5$ °K) and p-nitrotoluene ($T_m = 328.7$ °K).

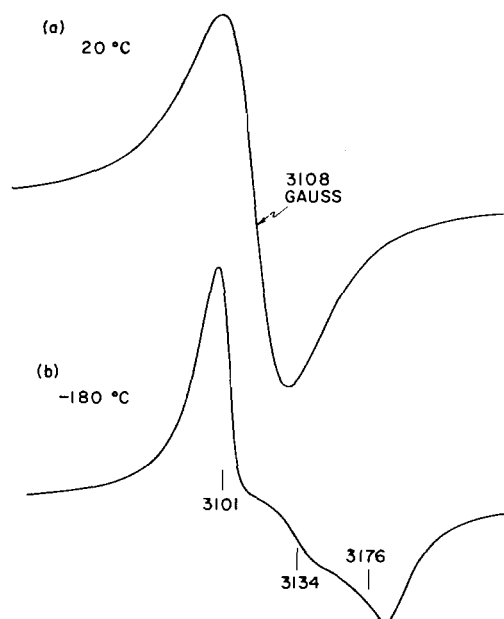Figure 1. The esr spectra of Cu^{2+} diluted into Co(NH₃)₆ CdCl₅ at (a) 20 °C and (b) −180 °C.

Results and Discussion

Figure 1 shows the electron spin resonance spectrum at (a) = 20 °C and (b) at −180 °C. The spectrum at −140 °C is identical with that at (b). It is clear that at room temperature, where the $CuCl_5^{3-}$ species is known to have 32 (D_{3h}) symmetry [2,8], the difference between g_{zz} and ($g_{xx} = g_{yy}$) is essentially nil since there is a single, symmetrical, esr line only (peak to peak width, about 300 gauss). The value of g = 2.20 we obtain for this species is in reasonable agreement with the value of 2.17 previously reported [1] for *undiluted* $Co(NH_3)_6CuCl_5$.

However, an attempt to sharpen the line(s) by cooling did not produce the desired effect; rather, one obtains (b). This latter spectrum is obviously due to a species for which there are three different g values (*i.e.*, $g_1 = 2.20$, $g_2 = 2.18$ and $g_3 = 2.15$; average = 2.183, which differs from the value of the same species at room temperature). The existence of *three* rather than *two* inflections in the spectra at −140 and −180 °C clearly indicates that the symmetry about the Cu^{2+} ion is no longer 32 (D_{3h}) since such a site symmetry is incompatible with the existence of three tensor components for g. Instead, the local symmetry at the Cu^{2+} site cannot have a principal axis of order

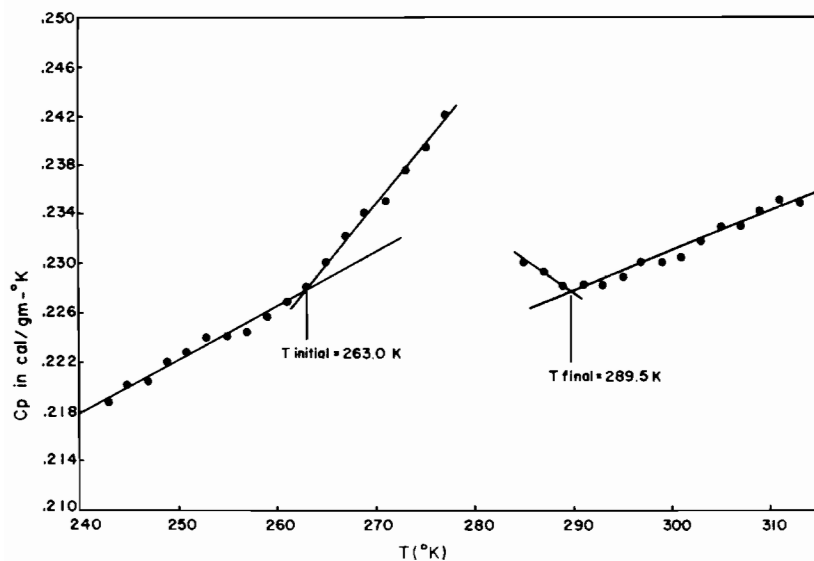Figure 2. Plot of the specific heat of $Co(NH_3)_6CuCl_5$ over the temperature range. The initial and final transition points (see Table II) were determined from this plot.
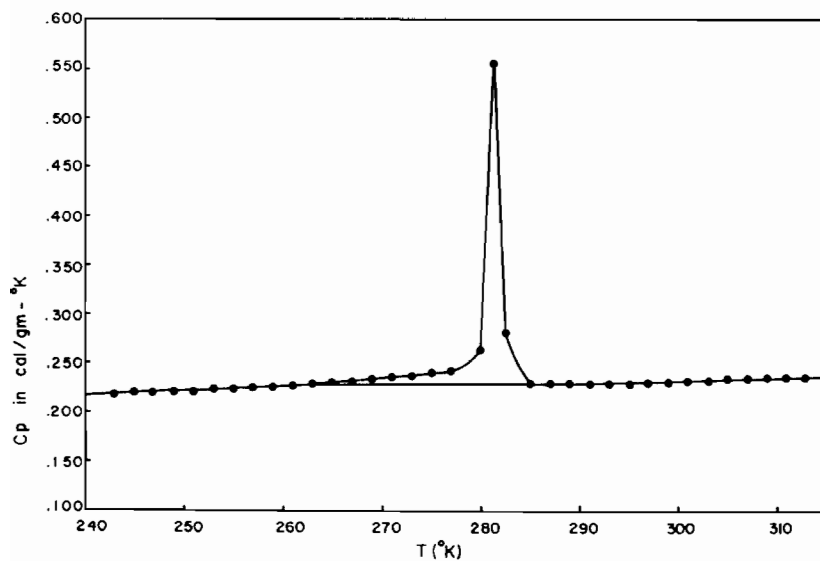

Figure 3. Plot of the specific heat data on a reduced scale to show the nature of the first order transition. The enthalpy of the transition (Table II) was determined using this plot.

higher than 2 (*i.e.*, xx $\neq$ yy $\neq$ zz). This observation suggested the existence of phase transitions in the temperature range used and differential thermal calorimetric measurements seemed desirable to check this suggestion.

Preliminary surveys of samples were carried out [10] which indicated that (a) there is a transition around $-10°C$, that (b) the transition was first order and (c) that identical results could be obtained from samples of pure $Co(NH_3)_6CuCl_5$, $Co(NH_3)_6CdCl_5$ as well as from samples of the former doped into the latter (the crystalline material used for the esr study). A detailed study of the Cu^{2+} salt was carried out and the results are displayed in graphical form in Figures 2 and 3 and the details of the specific heat data appear in Tables I and II.

It is clear from the measurements presented that there is a phase transition in the lattice of $Co(NH_3)_6$ (Cu, Cd)Cl_5 salts and that the point group symmetry

TABLE I. Specific Heat $Co(NH_3)_6$ $CuCl_5$.

T (K)	Cp (cal/gm K)
243	0.21875
245	0.22024
247	0.22048
249	0.22115
251	0.22270
253	0.22420
255	0.22425
257	0.22458
259	0.22572
261	0.22696
263	0.22800
265	0.23002
267	0.23238
269	0.23408
271	0.23505
273	0.23750
275	0.23947
277	0.24212
279	0.24234
281	–
283	–
285	0.23022
287	0.22931
289	0.22837
291	0.22846
293	0.22831
295	0.22870
297	0.23000
299	0.23018
301	0.32050
303	0.23172
305	0.23295
307	0.23303
309	0.23425
311	0.23504
313	0.23484
315	0.23559

TABLE II. Transition Data $Co(NH_3)_6CuCl_5$.

$T_{initial}$	263.0 K
T_{final}	289.5 K
$T_{transition}$	280.8 K
Enthalpy of Transition	1.332 cal/gm

that prevails at room temperature (32; D_{3h}) is no longer valid at or below the transition temperature of 280.8 °K. The esr measurements clearly indicate that the local symmetry at that site cannot have a principal axis of order higher than 2. Consequently, the interpretation of data, taken at temperatures lower than 280.8 °K, based on the assumption of a trigonal bipyramidal MCl_5^{3-} species is erroneous and the use of spectroscopic measurements [11] at liquid nitrogen temperatures for theoretical purposes [4–6] and for the interpretation of other experimental data [3, 7] (*i.e.*, susceptibility measurements, *etc.*) will have to await the elucidation of the low temperature structure.

Acknowledgements

References

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10 These measurements were carried out at the laboratory of Professor Ruben Rudman (Adelphi University) whom we thank for the use of the instrument and for instruction on its operation.
11 W. E. Hatfield, H. D. Bedon and S. M. Horner, *Inorg. Chem., 4,* 1181 (1965) who remarked in this paper that while Day (see ref. 4) found a single broad band in the visible region, apparently at room temperature, they found two bands by cooling to liquid nitrogen temperatures. They found the same results with the $Rh(NH_3)_6$ (III) as well as its cobalt analogue. This is obviously the result of a splitting of the energy levels of the pentachlorocuprate anion in the lower symmetry crystal field.