Inorganica Chimica Acta, 53 (1981) L69–L71
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Structure and Magnetic Properties of Some Mixed Metal $[(CH_3)_3NH]_3M_{2-x}M'_xCl_7$ Salts

S. A. ROBERTS and R. D. WILLETT

Department of Chemistry, Washington State University, Pullman, Wash. 99164, U.S.A.

Received July 31, 1980

Introduction

Several years ago the compound trimethylammonium heptachlorodimangonate(II), $(TMA)_3Mn_2Cl_7$, was synthesized in this laboratory [1]. The compound crystallizes in the hexagonal space group $P6_3mc$ and is analogous to, but of much higher symmetry than, the corresponding copper compound [2]. The crystal contains two distinct linear chains of metal–chloride anions, one of these chains being composed of tri-bridged $MnCl_6$ octahedra, while the other is a linear array of $MnCl_4^{2-}$ tetrahedra. This system was considered a good starting point for the preparation of a crystal with one dimensional magnetic properties. It was hoped, that by stoichiometrically replacing the paramagnetic metal ions in one chain, a better magnetic system than the tetramethylammonium tetrachloromanganate(II) salt could be obtained [3].

Sample Preparation and Physical Characteristics

Samples of M = M′ were generally prepared from stoichiometric quantities of TMACl [TMA = $(CH_3)_3NH^+$] and $MCl_2 \cdot nH_2O$ in aqueous, methanolic, or ethanolic solutions. For M = M′ ≠ Mn^{2+} or Cd^{2+} the salts grow as long hexagonal needles. The Mn^{2+} crystals are a pale pink, except when viewed from the ends of the crystal (the 0001 faces), where they appear a much deeper pink. This is due to the 'light pipe' effect of the sides of the crystals causing the weak Mn^{2+} luminescence to be preferentially transmitted parallel to the hexagonal crystal axis. This salt is also tribuluminescent, the crystals emitting pink light when crushed. The orange-brown crystals of the Cu^{2+} salt grow as much finer needles than the other salts, and are almost invariably twinned. They also are very hydroscopic, turning a pale yellow-green upon exposure to moist air.

Samples of M ≠ M′ salts prepared by growth from aqueous solution were invariably non-stoichiometric. The (Cd^{2+}, Cu^{2+}) system gave very nearly the pure Cd^{2+} salt with only a small amount of Cu^{2+} doped into the lattice (0.03%, determined by atomic absorption).

Structural Properties of $(TMA)_3M_xM'_{2-x}Cl_7$ Salts

The crystal structures of the M = M′ = Mn and M = M′ = Cu salts have been reported in the literature. The Mn salt is hexagonal, $P6_3mc$, with a = 14.509(19) Å and c = 6.485(7) Å [1]. The Cu salt, which is monoclinic, Cc, a = 14.30(3) Å, b = 24.67(4) Å, c = 6.30(2) Å and β = 92.52°, is closely related to the Mn salt [2], but the hexagonal symmetry is lost due to the Jahn–Teller distortion of the Cu^{2+} coordination sphere. Both salts assume polar structures. The trimethylammonium ions are ordered. The $CuCl_4^{2-}$ anion is reported to be nearly tetrahedral, but the magnitude of the thermal parameters indicate that the ion is more likely to have a typical D_{2d} distortion which is dynamically disordered at room temperature.

We have undertaken single crystal X-ray diffraction studies on two additional salts. The M = M′ = Cd salt is isomorphous with the corresponding Br salt; a = 14.863(3) Å and c = 6.869(1) Å. A complete structural analysis has been undertaken on $[(CH_3)_3NH]_3Cd_{1.3}Co_{0.7}Cl_7$. The space group is again $P6_3mc$ with a = 14.372(3) Å and c = 6.548(1) Å. The Co^{2+} ion was assumed to be located in the tetrahedral sites, while the Cd^{2+} ions were assumed to occupy the octahedral sites and the remainder of the tetrahedral sites. The occupancy of the tetrahedral sites was varied, and the least squares refinement of the positional, thermal, and occupancy factors proceeded directly to a final value of R_1 $(= \Sigma|F_o|-|F_c|/|F_o|)$ = 0.052 and of R_w $(= [\Sigma w|F_o - F|^2/\Sigma wF_o^2]^{1/2})$ = 0.050, where $w = 1/\sigma^2(F)$; and $\sigma^2(I) = TC + BC + (0.03)^2I^2$, where TC = total counts and BC = background counts. The occupancy factor for the tetrahedral site was greater than one. This corresponded to a Cd:Co ratio of 1.3:0.7, assuming the occupancy factor is given by the ratio $(X_{Co}Z_{Co} + X_{Cd}Z_{Cd})/Z_{Co}$, where X_i is the fraction of the ith component in the tetrahedral site and Z_i is the atomic number (Table I).

Magnetic and EPR Results

The powder EPR spectrum at 78 K of $(TMA)_3Cd_{1.3}Co_{0.7}Cl_7$ is a typical axial spectrum with $g_\parallel$ = 4.28 and $g_\perp$ = 2.37. No spectrum could be obtained at room temperatures due to the short relaxation time. However, the rather unusual observation of an EPR signal at 78 K indicates the presence of exchange

TABLE I. Structural Data for $[(CH_3)_3NH]_3Cd_{1.3}Co_{0.7}Cl_7$.

		a = 14.372(3)		
		c = 6.548(1)		
	x	y	z	occupancy
Cd	0	0	0	1/6
Co	1/3	2/3	0.1449(6)	0.206
Cl(1)	1/3	2/3	0.5061(14)	1/6
Cl(2)	0.4209(2)	−0.4209	0.0305(8)	1/2
Cl(3)	0.0826(2)	−0.0826	0.2514(7)	1/2
N	0.7907(4)	−0.7907	0.186(2)	1/2
C(1)	0.8263(7)	−0.8263(7)	0.372(3)	1/2
C(2)	0.3993(9)	0.1154(9)	0.063(2)	1

Bond Distances (Å)		Bond Angles (°)	
Cd–Cl(3)	2.635(3)	Cl(3)–Cd–Cl(3)	85.04(11)
Cd–Cl(3)′	2.622(3)	Cl(3)–Cd–Cl(3)′	94.69(3)
		Cl(3)′–Cd–Cl(3)′	85.58(11)
Co–Cl(1)	2.365(8)	Cl(1)–Co–Cl(2)	108.96(13)
Co–Cl(2)	2.304(2)	Cl(2)–Co–Cl(2)	109.98(13)
N–C(1)	1.50(2)	C(2)–N–C(2)	110.4(11)
N–C(2)	1.47(1)	C(2)–N–C(1)	110.2(7)
N–Cl(1)	3.306(7)	C(2)–N–Cl(1)	87.5(5)
N–Cl(2)	3.554(8)	C(2)–N–Cl(2)	90.1(5)
		C(1)–N–Cl(1)	147.1(6)
		C(1)–N–Cl(2)	79.6(5)

coupling causing a length of relaxation times, since spin diffusion processes in one dimensional systems lead to an enhancement of the long time correlations. Susceptibility measurements on a PAR magnetometer at 5 KOe from 2 to 150 K confirm the presence of weak antiferromagnetic coupling. A least squares fit to the Curie–Weiss law yields $\theta = -0.5$ K, with a Curie constant with high spin Co(II). The structural properties suggest one dimensional magnetic behavior between the tetrahedral sites. From θ, one estimates J/k to be of the order of −0.2 K. With axial site symmetry, the single ion Hamiltonian is simply $H - D S_z^2$. The condition $g_\parallel > g_\perp$ implies $D > 0$ (that is, the $m_s = \pm\frac{1}{2}$ levels lowest in energy). Thus for $|J| > D$, it is anticipated the system will behave as a one dimensional $S = \frac{1}{2}$ XY magnet. This has been confirmed by low temperature heat capacity measurements (0.2 to 1.0 K) on a $(TMA)_3CdCoCl_7$ sample by a melt technique [5]. This produces a random occupancy of octahedral and tetrahedral sites. The observed heat capacity was just that predicted for an $S = \frac{1}{2}$ XY linear chain with 50% occupancy of the tetrahedral sites by magnetic ions.

In order to determine which site the copper ion occupied in $(TMA)_3Cd_{2-x}Cu_xCl_7$, EPR spectra were taken at room and liquid nitrogen temperatures. At 77 K, the spectrum was that expected for a tetragonal copper occupying an octahedral site [6]. The g tensor was axial (the crystal symmetry is hexagonal), with $g_\parallel = 2.36$ and $g_\perp = 2.05$. Hyperfine splitting was resolved on the parallel resonance with $a_\parallel = 107$ G or 330 Mc/S, that expected for Cu^{2+} in an octahedral site. The room temperature spectrum showed one line, of width 100 G, centered on g = 2.159. This line is not isotropic, but has the shape a collapsing but not averaged signal would have.

Because of these contradictory results, the EPR spectra were taken at 20 °C intervals from 77 to 373 K. Representative spectra obtained are shown in Fig. 1.

This type of behavior was first observed by Bleaney [7] in the EPR of Cu^{2+} doped into zinc fluoroscilicate. Copper ion geometries are not regular. In the case of $CuCl_6$, the copper geometry takes on the familiar 4 + 2 coordination. There are four planar, normal length Cu–Cl bonds, and two elongated axial Cu–Cl bonds. At low temperatures, in this case 77 K, the copper ion coordination is frozen into the lattice in one of three equivalent sites about the crystallographic three-fold axis of the chain. As the temperature is increased, a previously latent vibration can occur and the three orientations of the distortion

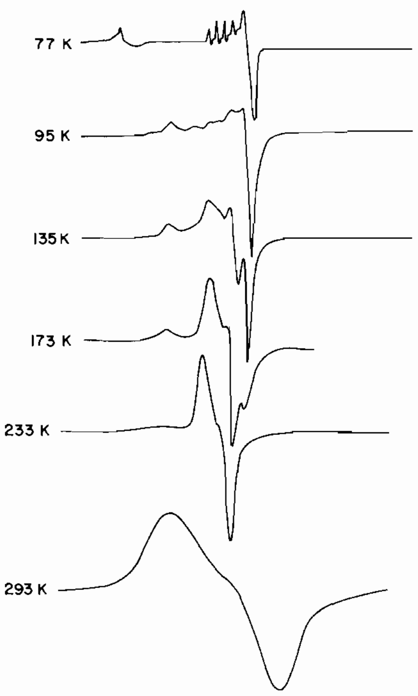

Fig. 1. Representative EPR spectra for Cu^{2+} doped into the $(TMA)_3Cd_2Cl_7$ lattice. The scale of the 78 K spectrum is 1/3 that of the intermediate temperature spectra, while the scale of the 293 K spectrum is 4.5 times that of the intermediate spectra.

will begin to interconvert. With increasing temperature, this conversion will occur more often, until, when it is of a frequency faster than that corresponding to the EPR line width, the signal will collapse into an isotropic line. As seen in the figure, this onset of motion occurs over a temperature range of 200 degrees.

The line shapes obtained are qualitatively similar to those calculated by Hudson [8] for the tris-ethylenediaminecopper(II) ion spectra reported by Kokoszka [9], but more structure is apparent. This may be due to the averaging of the different copper hyperfine lines of different rates. Another possibility is that it is due to the formation of Cu_2Cl_9 dimers within the chain. It has recently been shown [10] that manganese ions doped into cadmium salts preferentially dimerize, even at concentrations of 0.1 ppt. The observation of the $\Delta m_s = \pm 2$ line at low temperatures, as shown in the spectra at 77 K, encourages this conclusion.

References

1 R. E. Caputo, S. A. Roberts, R. D. Willett, and B. C. Gerstein, *Inorg. Chem.*, *5*, 820 (1976).
2 R. M. Clay, P. Murray-Rust and J. Murray-Rust, *J. Chem. Soc. Dalton*, 595 (1973).
3 B. Morosin and E. J. Graeber, *Acta Cryst.*, *23*, 776 (1967).
4 P. A. Daoud, R. Perret, and Y. Dusausoy, *Acta Cryst.*, *B35*, 2718 (1979).
5 L. J. de Jongh and H. Algra, private communication.
6 J. H. E. Griffiths and J. H. M. Thornley, *Proc. Phys. Soc. (London)*, *79*, 1263 (1961).
7 B. Bleaney and K. D. Bowers, *Proc. Phys. Soc. (London)*, *A65*, 667 (1952).
8 A. Hudson, *Mol. Phys.*, *10*, 575 (1966).
9 H. C. Allen, G. F. Kokoszka, R. G. Inskeep, *J. Am. Chem. Soc.*, *86*, 1023 (1964).
10 G. A. McPherson, *J. Am. Chem. Soc.*, *100*, 467 (1978).