

## Synthesis and Magnetic Properties of Manganese(II) Salicylate Dihydrate

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Salicylates were among the first drugs of the anti-pyretic and antirheumatic agents and still are very commonly used. Although salicylic acid has anti-pyretic and antirheumatic activities, it is too toxic to be used as such [1]. One possible means of lowering the toxicity and retaining some desirable properties is to form transition metal salicylates. For example copper salicylate has been used in the treatment of rheumatoid and degenerative diseases [2]. It is very likely that other transition-metal complexes of salicylic acid are also therapeutically valuable. In this article the synthesis and magnetic properties of the title compound, manganese salicylate, are reported.

### Experimental

For the preparation of the manganese complex, salicylic acid (2.76 g, 0.02 mol) was allowed to dissolve in an aqueous solution of potassium bicarbonate (2.00 g, 0.02 mol). To this stirring solution was added an aqueous solution of manganous chloride tetrahydrate (1.98 g, 0.01 mol). Minimum quantities of water were used for dissolutions. The mixture was allowed to stir for thirty minutes. The solution was then filtered and the filtrate allowed to evaporate in a desiccator over sulfuric acid. After two weeks the crystals which formed were collected on a filter and washed several times with ice cold water and then dried for two days over calcium sulfate. *Anal.* Calcd. for  $MnC_{14}H_{14}O_8$ : Mn, 15.04; C, 46.04; H, 3.87. Found: Mn, 14.82; C, 46.03; H, 3.85%. The magnetic susceptibility was determined as a function of temperature with a Faraday system [3]. Mercury tetrathiocyanatocobalt(II) was used as the magnetic susceptibility standard [4], and appropriate diamagnetic corrections were estimated from Pascal's constants [5]. EPR spectra were obtained using a Varian E109E spectrometer operating near 9.5 GHz. The field was calibrated using diphenylpicrylhydrazyl (DPPH) for which  $g = 2.0036$ . Cylindrical quartz sample tubes and a Varian E-231 rectangular cavity were employed. Infrared spectra were obtained by using a Nicolet MX-1 instrument. Nujol mull and potassium bromide disc techniques were employed.

### Results and Discussion

The elemental analyses indicate the presence of two moles of salicylate and two moles of water per one mole of manganese, *i.e.*  $Mn(\text{salicylate})_2 \cdot (H_2O)_2$ . The comparison of the IR spectra of salicylic acid and the manganese(II) compound confirmed the presence of salicylate in the compound. For the compound the antisymmetric COO stretch occurs at  $1631\text{ cm}^{-1}$  and the symmetric stretch at  $1404\text{ cm}^{-1}$ . The absorption due to water was found at  $3400\text{ cm}^{-1}$ . The neutral compound dissociates in water and methanol yielding molar conductivities of 45.0 and  $40.2\text{ mho}\cdot\text{cm}^2\cdot\text{mol}^{-1}$  at  $0^\circ\text{C}$ , respectively. This appreciable dissociation may be expected due to no ligand field stabilization energy for the high-spin Mn(II).

EPR spectra were recorded on polycrystalline samples and on pyridine solutions. For the polycrystalline sample only a broad featureless absorption at  $g = 2.00$  was observed. For the case of an axial distortion of the octahedral field, the magnitude of the zero field splitting is expressed by the axial field splitting parameter,  $D$ . The spin Hamiltonian [6] is

$$H = g\beta H \cdot S + D[S_z^2 - \frac{1}{3}S(S+1)] + AS \cdot I$$

In this equation  $H$  is the magnetic field vector,  $g$  is the spectroscopic splitting factor,  $\beta$  is the Bohr magneton,  $A$  is manganese nuclear hyperfine splitting constant,  $S$  is the electronic spin vector,  $I$  is the nuclear spin vector,  $S = 5/2$ , and  $S_z$  is the diagonal spin operator. In the spectrum for the polycrystalline sample only the  $\Delta M_S = \frac{1}{2} \rightarrow -\frac{1}{2}$  transition is observed since the angular dependence of the  $\Delta M_S = \pm 5/2 \rightarrow \pm 3/2$  and  $\pm 3/2 \rightarrow \pm 1/2$  transitions broadens these peaks beyond resolvability. This line is further split into six lines by the nuclear hyperfine splitting due to  $^{55}\text{Mn}$  ( $I = 5/2$ ); however, due to dipolar broadening only the single broad absorption is observed. As shown in Fig. 1 the six lines due to the nuclear hyperfine splitting are clearly resolved for the pyridine solution spectrum. This absorption is also centered at  $g = 2.00$ . Due to the remoteness of the excited states,  $g$ -values for high-spin  $3d^5$  are expected to be very near the free-electron value. From the spectrum,  $A_{\text{avg}} = 0.00085\text{ cm}^{-1}$  and  $D = 0.022\text{ cm}^{-1}$ .

The experimental and calculated magnetic susceptibility data are shown in Table I. The data were described by the Curie-Weiss law,

$$\chi_M^{\text{corr}} = \frac{g^2 N \beta^2}{3K(T - \theta)} S(S+1) + \chi_M^{\text{T.L.P.}}$$

where all the symbols have their usual meaning. By use of a least-squares computer program the experimental results are best fit with  $g = 1.99$ ,  $\chi_M^{\text{T.L.P.}} = 94 \times 10^{-6}$  cgs units,  $\theta = 0$ , and  $\mu_{\text{eff}} = 5.90$  B.M. The

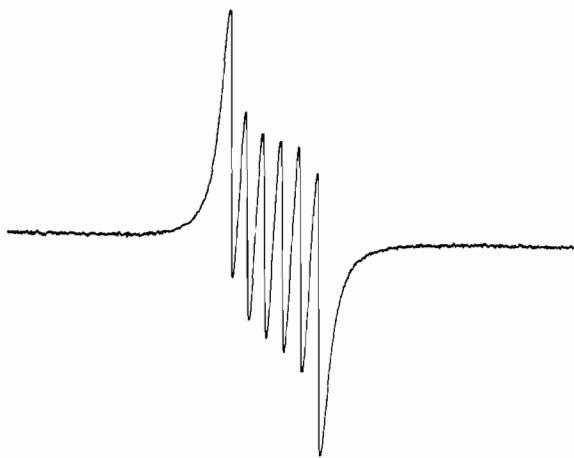


Fig. 1. The EPR spectrum of manganese(II) salicylate dihydrate in pyridine solution at room temperature.

equation,  $\mu_{\text{eff}} = 2.83 (\chi_M^{\text{corr}} \cdot T)^{1/2}$ , was used to calculate the magnetic moments. The standard deviation in  $\chi_M^{\text{corr}}$  was  $199 \times 10^{-6}$  cgs units. The g-value is in excellent agreement with that obtained from the EPR measurements. The ground term for the octahedral configuration is  ${}^6A_{1g}$  [7], and therefore there should be no reduction of the moment below the spin-only value by spin-orbit coupling with higher ligand field terms. The moments are, indeed, found to be very close to the spin-only value of 5.92 B.M. Although no T.I.P. is expected for this ground term,  $94 \times 10^{-6}$  was found; however, this amount may be disregarded in view of the standard deviation of  $199 \times 10^{-6}$ . The standard deviation of  $199 \times 10^{-6}$  appears to be large, but is very small when compared to the magnetic susceptibilities.

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TABLE I. Experimental and Calculated Magnetic Data.

Temp. (K)	$10^6 \chi_M^{\text{corr}}$ (exp.) (B.M.)	$10^6 \chi_M^{\text{corr}}$ (calc.) (B.M.)
77	56,398	56,349
88	49,071	49,317
96	45,214	45,215
107	40,576	40,577
114	38,341	38,091
130	33,417	33,414
147	30,166	29,561
153	28,351	28,405
166	26,080	26,188
176	24,857	24,706
184	23,651	23,636
198	22,015	21,971
212	20,412	20,526
225	19,257	19,346
234	18,550	18,605
241	17,593	18,068
254	17,102	17,148
263	16,522	16,564
275	15,906	15,848
284	15,333	15,346
295	14,847	14,778

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#### References

- 1 A. Korolkovas and J. H. Burckhalter, 'Essentials of Medicinal Chemistry', John Wiley, New York, 1976.
- 2 J. R. J. Sorenson and W. Hangarter, *Inflammation*, 2, 217 (1977).
- 3 P. E. Rush, J. D. Oliver, G. D. Simpson and G. O. Carlisle, *J. Inorg. Nucl. Chem.*, 37, (1975).
- 4 H. St-Räde, *J. Phys. Chem.*, 77, 424 (1973).
- 5 E. König, *Magnetic Properties of Transition Metal Compounds*, Springer-Verlag, Berlin, 1966.
- 6 H. A. Kuska, F. M. D'Itri and A. I. Popov, *Inorg. Chem.*, 5, 1272 (1966).
- 7 R. A. Palmer, M. C. Yang and J. C. Hempel, *Inorg. Chem.*, 17, 1200 (1978).