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# SINGLE CRYSTAL X-RAY STRUCTURE OF $[GALVINOXYL]_x$-$[HYDROGALVINOXYL]_{1-x}$ ($x = 0.85 \pm 0.02$) AT 20 AND 203 K

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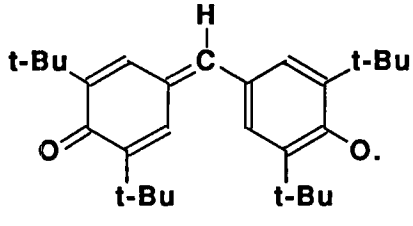
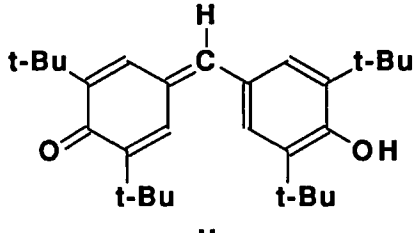
Abstract Galvinoxyl undergoes a first order phase transition at 85 K with a concomitant transition from a ferromagnetic-coupled to essentially diamagnetic susceptibility. Attempts to obtain the single crystal x-ray structure below 85 K have failed due to disintegration of the crystals. Solid solutions of galvinoxyl/hydrogalvinoxyl, however, suppress the phase transition. The structures of $[galvinoxyl]_x$-$[hydrogalvinoxyl]_{1-x}$ ($x = 0.85 \pm 0.02$) at $20 \pm 5$ and $203 \pm 2$ K are described. The motif and atomic coordinates are essentially identical to those previously reported for the room temperature structure.

## INTRODUCTION

Galvinoxyl, 2,6-di-*t*-butyl-4-(3,5-di-*t*-butyl-4-oxycyclohexa-2,5-dienylidene methyl)phenoxy radical, **I**, is an unique organic molecule as it exhibits ferromagnetic coupling in the solid state.[1] Below 85 K, **I**, however, undergoes




**I**




**II**

a first order phase transition to a very weakly magnetic state.[1a,2] The structural consequences of this spin-pairing transformation are unknown. Kinoshita and coworkers have shown that the phase transition can be

suppressed by forming a solid solution of galvinoxyl with hydrogalvinoxyl, **II**, with 6:1 galvinoxyl:hydrogalvinoxyl.

## PREPARATION AND PURIFICATION OF GALVINOXYL

In order to obtain pure galvinoxyl, we have attempted to purify the commercial sample (Aldrich) in several different ways. Sample **A** are dark blue crystalline needles which grown from acetonitrile solution at -20 C. Sample **B**, a microcrystalline solid, was recrystallized from *n*-octane twice in freezer. Sample **C** was obtained by stirring the solution of galvinoxyl in *n*-octane with lead peroxide and a trace of calcium hydride for three hours under nitrogen twice prior to recrystallization from the *n*-octane solution in a freezer after careful filtration. Upon comparison of the magnetic susceptibility data (*vide infra*) with those reported by Kinoshita and co-workers for a series of differing solid solutions of the galvinoxyl:hydrogalvinoxyl[1b] the composition of **A** was estimated to be $[\text{galvinoxyl}]_x[\text{hydrogalvinoxyl}]_{1-x}$ ($x = 0.85 \pm 0.02$).

## STRUCTURE

The structure of sample **A**, galvinoxyl/hydrogalvinoxyl, has been determined by x-ray crystallography at 20 and 203 K. The structural parameters are virtually equivalent to those previously reported at room temperature by Williams.[3] The resolution, however, is significantly improved and the coordinates are now refined anisotropically and lower R values are achieved. A labeling diagram and stereoview are presented in Figures 1 and 2, respectively. Tables 1 summarizes the crystal data and structure determination parameters, whereas Tables 2 - 8 contain, atomic coordinates, anisotropic thermal parameters, bond distances and angles.

The galvinoxyl is a nearly planar molecule with a two-fold rotation axis through the methine C-H moiety. A small twist angle between two rings (18.7°) was observed. The phenyl rings are planar within experimental error. The shorter C(3)-C(4) and C(6)-C(7) bond distances are indicative of the quinoid feature. Both C(5)-O(1) and C(1)-C(2) distances are between single and double bond lengths.

The molecules pack along the c-axis and form sheets stacked along the *a*-axis. Intermolecular distances shorter than sum of the van der Waals

contacts were not observed. The two phenyl rings remained slightly twisted and nearly planar in the molecule even below the phase transition temperature. On the other hand, a large twist angle (47.03°) between two phenyl rings and the dimerization of two radicals were found in azagalvinoxyl, the nitrogen analog of galvinoxyl.[4] The low temperature structure determinations confirmed that the phase transition of galvinoxyl was suppressed in the existence of hydrogalvinoxyl.

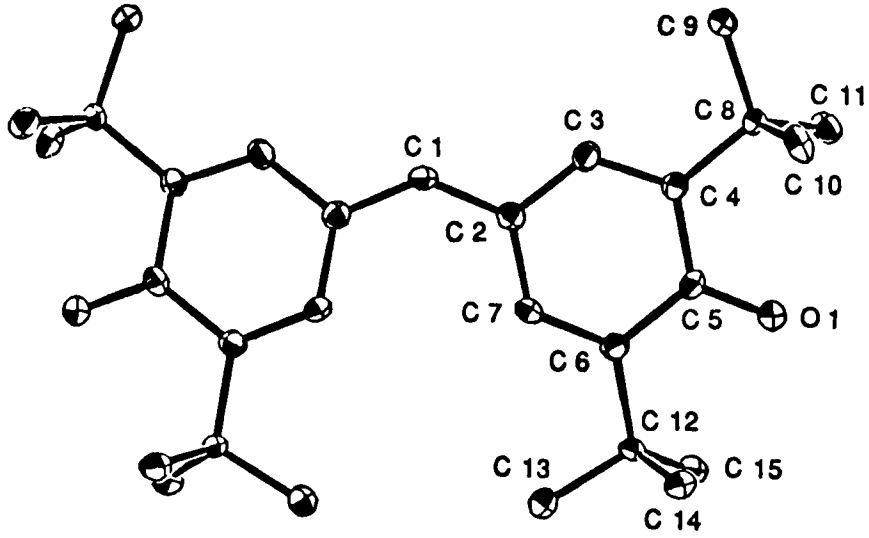



FIGURE 1. Atom labeling diagram of galvinoxyl, **I**.

TABLE 1. Crystal Data and Structure Determination Parameters for $[galvinoxyl]_x[hydrogalvinoxyl]_{1-x}$ (x = 0.85 ± 0.02)

| | 20 ± 5 K | 70 ± 5 K | 203 ± 2 K |
|---|---|---|---|
| Formula Weight | 422.65 | | 422.65 |
| Crystal System | monoclinic | | monoclinic |
| Space Group | *C2/c* (No.15) | | *C2/c* (No.15) |
| Crystal Dimension, mm | 0.40x0.20x0.30 | | 0.25x0.18x0.48 |
| *a*, Å | 23.56 (1) | 23.48 (1) | 23.600 (10) |
| *b*, Å | 10.622 (4) | 10.661 (2) | 10.786 (1) |
| *c*, Å | 10.459 (5) | 10.466 (3) | 10.576 (4) |
| *β*, deg | 106.46 (1) | 106.27 (1) | 106.41 (2) |
| Z | 4 | | 4 |
| V, Å$^3$ | 2510.75 | 2514.9 | 2578.1 |
| ρ(calc'd), g cm$^{-3}$ | 1.12 | | 1.089 |

| | | |
|---|---|---|
| Radiation, λ, cm | Mo $K_\alpha$, 0.7107 | Mo $K_\alpha$, 0.7107 |
| Diffractometer | Huber [a] | CAD4 |
| Scan Mode, Speed (deg/min) | θ-2θ, 4.5 | ω, 1.80 - 5.00 |
| 2θ range, deg | 1- 50 | 3.6 - 54.8 |
| Total Data Collected | 4425 | 2661 |
| Unique Data Used, $I > 3\sigma(I)$ | 1313 | 683 |
| Parameters Refined | 141 | 141 |
| Final diff map, $e^-/Å^3$ | 0.26 - 0.13 | 0.20 |
| R[b] | 0.053 | 0.059 |
| $R_w$[c] | 0.061 | 0.053 |

[a] Automated at UCLA [b] $\Sigma||F_o|-|F_c||\Sigma|F_o|$ [c] $(\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|)^{2)^{1/2}}$

TABLE 2 Fractional Coordinates and Isotropic Thermal Parameters for $[galvinoxyl]_x[hydrogalvinoxyl]_{1-x}$ ($x = 0.85 \pm 0.02$) at 20 K

| Atom | x | y | z | $10^4xU$ [a] |
|---|---|---|---|---|
| O(1) | 0.1752(1) | 0.6420(2) | 0.6741(2) | 269(18) |
| C(1) | 0.0000 | 0.4547(4) | 0.2500 | 222(33) |
| C(2) | 0.0409(1) | 0.5074(3) | 0.3632(3) | 248(24) |
| C(3) | 0.0836(1) | 0.4235(3) | 0.4457(3) | 239(24) |
| C(4) | 0.1292(1) | 0.4636(3) | 0.5505(3) | 212(23) |
| C(5) | 0.1339(1) | 0.5999(3) | 0.5811(3) | 227(23) |
| C(6) | 0.0883(1) | 0.6865(3) | 0.5004(3) | 203(23) |
| C(7) | 0.0435(1) | 0.6374(3) | 0.3992(3) | 211(23) |
| C(8) | 0.1768(1) | 0.3737(3) | 0.6318(3) | 187(23) |
| C(9) | 0.1615(1) | 0.2354(3) | 0.5905(3) | 272(25) |
| C(10) | 0.2365(1) | 0.4048(3) | 0.6093(3) | 316(25) |
| C(11) | 0.1807(1) | 0.3825(3) | 0.7817(3) | 267(24) |
| C(12) | 0.0939(1) | 0.8287(3) | 0.5287(3) | 188(23) |
| C(13) | 0.0455(1) | 0.9032(3) | 0.4279(3) | 255(24) |
| C(14) | 0.1538(1) | 0.8763(3) | 0.5142(3) | 276(25) |
| C(15) | 0.0890(1) | 0.8562(3) | 0.6702(3) | 265(24) |
| H(1) | 0.0000 | 0.3575 | 0.2500 | |
| H(3) | 0.0778 | 0.3298 | 0.4282 | |
| H(7) | 0.0119 | 0.6972 | 0.3473 | |
| H(9) | 0.1891 | 0.1754 | 0.6525 | |
| H(9') | 0.1655 | 0.2196 | 0.4968 | |
| H(9") | 0.1202 | 0.2221 | 0.5931 | |

| | | | |
|---|---|---|---|
| H(10) | 0.2649 | 0.3341 | 0.6460 |
| H(10') | 0.2519 | 0.4844 | 0.6548 |
| H(10") | 0.2318 | 0.4143 | 0.5122 |
| H(11) | 0.2155 | 0.3341 | 0.8367 |
| H(11') | 0.1437 | 0.3500 | 0.7995 |
| H(11") | 0.1849 | 0.4736 | 0.8058 |
| H(13) | 0.0479 | 0.9966 | 0.4481 |
| H(13') | 0.0045 | 0.8737 | 0.4267 |
| H(13") | 0.0521 | 0.8873 | 0.3397 |
| H(14) | 0.1588 | 0.9704 | 0.5331 |
| H(14') | 0.1576 | 0.8608 | 0.4228 |
| H(14") | 0.1832 | 0.8281 | 0.5829 |
| H(15) | 0.0942 | 0.9465 | 0.6918 |
| H(15') | 0.1208 | 0.8066 | 0.7385 |
| H(15") | 0.0488 | 0.8247 | 0.6709 |

[a] $U_{eq} = [1/(6\pi^2)]\Sigma\Sigma\beta_{ij}a_ia_j$

TABLE 3 Fractional Coordinates, x$10^4$ Å, and Isotropic Thermal Parameters for [galvinoxyl]$_x$[hydrogalvinoxyl]$_{1-x}$ ($x = 0.85 \pm 0.02$) at 203 K

| Atom | x | y | z | $B_{ISO}$, Å$^2$ |
|---|---|---|---|---|
| O(1) | 1703(2) | 6391(4) | 6759(4) | 6.3(2)' |
| C(1) | 0(0) | 4635(7) | 2500(0) | 3.4(3)' |
| C(2) | 405(3) | 5122(6) | 3620(6) | 2.5(2)' |
| C(3) | 830(3) | 4305(6) | 4431(6) | 2.7(2)' |
| C(4) | 1279(3) | 4670(6) | 5461(6) | 2.5(2)' |
| C(5) | 1317(3) | 6004(7) | 5808(6) | 3.2(2)' |
| C(6) | 871(3) | 6866(6) | 4982(6) | 2.4(2)' |
| C(7) | 434(3) | 6401(6) | 3976(5) | 2.5(2)' |
| C(8) | 1749(3) | 3798(6) | 6254(5) | 2.7(2)' |
| C(9) | 1631(3) | 2456(8) | 5775(7) | 6.2(3)' |
| C(10) | 2349(3) | 4154(8) | 6110(7) | 5.5(3)' |
| C(11) | 1769(3) | 3791(7) | 7702(6) | 5.0(3)' |
| C(12) | 927(3) | 8253(6) | 5295(6) | 3.0(2)' |
| C(13) | 469(3) | 9009(6) | 4294(6) | 4.4(3)' |
| C(14) | 1529(3) | 8721(6) | 5225(7) | 5.2(3)' |

| | | | | |
|---|---|---|---|---|
| C(15) | 863(3) | 8521(6) | 6660(7) | 5.3(3)' |
| H(1) | 0 | 3696 | 2500 | 3.5 |
| H(3) | 791 | 3441 | 4243 | 3.5 |
| H(7) | 133 | 6941 | 3490 | 3.5 |
| H(9) | 1930 | 1942 | 6296 | 3.5 |
| H(9') | 1620 | 2408 | 4885 | 3.5 |
| H(9") | 1254 | 2210 | 5897 | 3.5 |
| H(10) | 2637 | 3597 | 6597 | 3.5 |
| H(10') | 2439 | 4978 | 6432 | 3.5 |
| H(10") | 2343 | 4125 | 5203 | 3.5 |
| H(11) | 2060 | 3234 | 8147 | 3.5 |
| H(11') | 1387 | 3536 | 7775 | 3.5 |
| H(11") | 1849 | 4607 | 8031 | 3.5 |
| H(13) | 516 | 9868 | 4519 | 3.5 |
| H(13') | 82 | 8749 | 4309 | 3.5 |
| H(13") | 521 | 8884 | 3445 | 3.5 |
| H(14) | 1562 | 9584 | 5413 | 3.5 |
| H(14') | 1564 | 8588 | 4348 | 3.5 |
| H(14") | 1832 | 8281 | 5829 | 3.5 |
| H(15) | 906 | 9385 | 6823 | 3.5 |
| H(15') | 1168 | 8085 | 7286 | 3.5 |
| H(15") | 488 | 8247 | 6709 | 3.5 |

TABLE 4 Anisotropic Thermal Parameters, $10^4$ Å, for $[galvinoxyl]_x[hydrogalvinoxyl]_{1-x}$ ($x = 0.85 \pm 0.02$) at 20 K

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| O(1) | 49(2) | 287(18) | 438(25) | 4(5) | -21(6) | -2(17) |
| C(1) | 45(5) | 178(34) | 387(48) | 0 | 22(12) | 0 |
| C(2) | 32(3) | 264(25) | 389(35) | 10(7) | 30(8) | 17(23) |
| C(3) | 36(3) | 285(26) | 348(34) | -10(7) | 21(8) | -39(23) |
| C(4) | 30(3) | 277(25) | 282(31) | -4(7) | 29(8) | -19(23) |
| C(5) | 33(3) | 276(26) | 324(33) | -9(7) | 23(8) | -66(24) |
| C(6) | 38(3) | 234(25) | 289(32) | -8(7) | 29(8) | 4(22) |
| C(7) | 35(3) | 209(24) | 336(33) | 4(7) | 27(8) | 51(23) |
| C(8) | 40(3) | 218(25) | 276(32) | 6(7) | -7(8) | -39(22) |
| C(9) | 51(4) | 248(26) | 478(36) | 13(8) | -19(9) | -10(25) |
| C(10) | 40(3) | 459(29) | 392(34) | 32(8) | 24(9) | 143(26) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(11) | 47(3) | 328(26) | 365(33) | 20(8) | 36(8) | 42(24) |
| C(12) | 44(3) | 161(24) | 326(33) | 14(7) | 0(8) | 3(22) |
| C(13) | 46(4) | 297(27) | 376(33) | 5(8) | 11(8) | -44(24) |
| C(14) | 49(3) | 251(26) | 464(35) | -4(8) | 25(9) | -27(24) |
| C(15) | 59(4) | 272(25) | 405(34) | 0(8) | 24(8) | 6(25) |

TABLE 5 Anisotropic Thermal Parameters, $10^3$ Å, for $[galvinoxyl]_x[hydrogalvinoxyl]_{1-x}$ ($x = 0.85 \pm 0.02$) at 203 K

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| O(1) | 79(4) | 52(4) | 72(4) | 5(3) | -39(3) | -15(3) |
| C(1) | 47(7) | 14(6) | 66(8) | 0(0) | 8(6) | 0(0) |
| C(2) | 23(4) | 38(5) | 29(4) | -10(3) | 2(3) | -3(4) |
| C(3) | 31(4) | 34(4) | 36(4) | 6(4) | 7(3) | 8(4) |
| C(4) | 34(4) | 37(5) | 24(4) | 7(3) | 8(3) | 3(3) |
| C(5) | 37(5) | 48(5) | 34(4) | -3(4) | 2(3) | 1(4) |
| C(6) | 31(4) | 36(4) | 26(4) | 1(3) | 11(3) | -3(3) |
| C(7) | 28(4) | 32(4) | 33(4) | 4(3) | 6(3) | 2(3) |
| C(8) | 32(4) | 43(5) | 25(4) | 11(4) | 1(3) | -3(3) |
| C(9) | 78(6) | 61(6) | 73(6) | 30(5) | -20(4) | -8(5) |
| C(10) | 35(5) | 108(7) | 70(5) | 31(5) | 20(4) | 34(5) |
| C(11) | 55(5) | 84(6) | 46(4) | 30(5) | 9(4) | 13(4) |
| C(12) | 42(5) | 38(4) | 27(4) | 2(4) | 2(4) | -5(3) |
| C(13) | 71(6) | 35(5) | 53(5) | 3(4) | 6(4) | -9(4) |
| C(14) | 69(6) | 34(5) | 84(6) | -10(4) | 5(4) | -16(4) |
| C(15) | 92(6) | 45(5) | 59(5) | 7(4) | 15(4) | -2(4) |

TABLE 6 Intermolecular Bond Distance, Å, for $[galvinoxyl]_x[hydrogalvinoxyl]_{1-x}$ ($x = 0.85 \pm 0.02$)

| Bond | Distance at 203 K, Å | Distance at 20 K, Å |
|---|---|---|
| O(1)-C(5) | 1.224 (6) | 1.248 (3) |
| C(1)-C(2) | 1.397 (6) | 1.413 (4) |
| C(2)-C(3) | 1.424 (8) | 1.435 (4) |
| C(2)-C(7) | 1.425 (7) | 1.428 (4) |
| C(3)-C(4) | 1.346 (7) | 1.368 (4) |
| C(4)-C(5) | 1.479 (8) | 1.480 (4) |
| C(4)-C(8) | 1.514 (7) | 1.534 (4) |
| C(5)-C(6) | 1.488 (8) | 1.483 (4) |

| | | |
|---|---|---|
| C(6)-C(7) | 1.350 (7) | 1.369 (4) |
| C(6)-C(12) | 1.527 (8) | 1.538 (4) |
| C(8)-C(9) | 1.530 (10) | 1.545 (4) |
| C(8)-C(10) | 1.516 (9) | 1.527 (4) |
| C(8)-C(11) | 1.519 (8) | 1.547 (4) |
| C(12)-C(13) | 1.519 (8) | 1.535 (4) |
| C(12)-C(14) | 1.529 (9) | 1.547 (5) |
| C(12)-C(15) | 1.521 (8) | 1.545 (4) |

TABLE 7 Bond Angles, deg, for $[galvinoxyl]_x[hydrogalvinoxyl]_{1-x}$ ($x = 0.85 \pm 0.02$)

| Atoms | Angle, deg, at 203 K | Angle, deg, at 20 K |
|---|---|---|
| O(1)-C(5)-C(4) | 120.9 (6) | 120.8(2) |
| O(1)-C(5)-C(6) | 120.6 (6) | 120.0(2) |
| C(2)-C(1)-C(2)[a] | 136.0 (9) | 133.3(2) |
| C(1)-C(2)-C(3) | 118.4 (6) | 116.9(2) |
| C(1)-C(2)-C(7) | 123.8 (6) | 124.8(2) |
| C(3)-C(2)-C(7) | 117.7 (5) | 118.1 (2) |
| C(2)-C(3)-C(4) | 124.5 (6) | 123.1 (2) |
| C(3)-C(4)-C(5) | 117.6 (6) | 118.1(2) |
| C(3)-C(4)-C(8) | 123.6 (6) | 122.3(2) |
| C(5)-C(4)-C(8) | 118.8 (5) | 119.4(2) |
| C(4)-C(5)-C(6) | 118.5 (5) | 119.0(2) |
| C(5)-C(6)-C(7) | 119.2 (6) | 118.6 (2) |
| C(5)-C(6)-C(12) | 118.6 (5) | 119.4(2) |
| C(7)-C(6)-C(12) | 122.2 (6) | 121.9(2) |
| C(2)-C(7)-C(6) | 122.4 (6) | 122.5 (2) |
| C(4)-C(8)-C(9) | 111.4 (5) | 111.1(2) |
| C(4)-C(8)-C(10) | 110.3 (5) | 109.9 (2) |
| C(4)-C(8)-C(11) | 111.7 (5) | 110.3(2) |
| C(9)-C(8)-C(10) | 107.1 (6) | 108.3 (2) |
| C(9)-C(8)-C(11) | 106.3 (5) | 106.4(2) |
| C(10)-C(8)-C(11) | 109.8 (5) | 110.5(2) |
| C(6)-C(12)-C(13) | 111.9 (6) | 111.5 (2) |
| C(6)-C(12)-C(14) | 109.7 (6) | 109.4(2) |
| C(6)-C(12)-C(15) | 111.4 (5) | 110.1(2) |
| C(13)-C(12)-C(14) | 106.1 (6) | 106.5(2) |

| | | |
|---|---|---|
| C(13)-C(12)-C(15) | 108.5 (6) | 108.5(2) |
| C(14)-C(12)-C(15) | 109.0 (6) | 110.5 (2) |

[a] -x, y, 1/2 - z

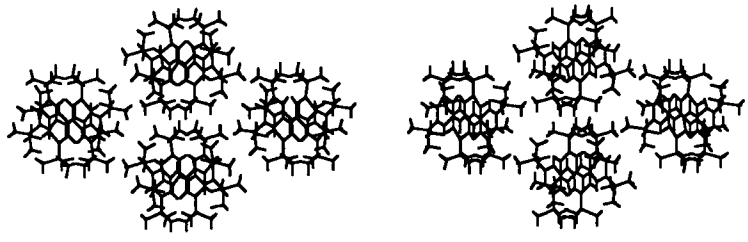


FIGURE 2. Stereoview of the unit cell of for $[galvinoxyl]_x[hydrogalvinoxyl]_{1-x}$ ($x = 0.85 \pm 0.02$)

TABLE 8 Nonbonding Bond Distance, Å, for $[galvinoxyl]_x[hydrogalvinoxyl]_{1-x}$ ($x = 0.85 \pm 0.02$)

| Atoms | Distance at 20 K, Å | Distance at 203 K, Å |
|---|---|---|
| O(1)···C(10) | 3.073 (4) | 3.032 (9) |
| O(1)···C(11) | 2.966 (3) | 2.961 (9) |
| O(1)···C(14) | 2.961 (3) | 2.953 (8) |
| O(1)···C(15) | 3.042 (4) | 3.014 (9) |

The variation of cell constants with temperature is presented in Fig. 3. Constants *b* and *c* increase monotonically with increasing temperature whereas *a* and $\beta$ are substantially larger ar 20 K than 70 K.

## MAGNETIC SUSCEPTIBILITY

The magnetic susceptibilities of the commercially available sample as well as after purification by several methods were measured by the Faraday method[5] between 2.2 and 320 K, Fig. 4. The data was fit to the Curie-Weiss expression, $\chi = C/(T - \theta)$, and C, $\theta$, radical concentration, and transition temperatures, $T_{MAX}$, are summarized in Table 9.

As earlier described,[1,2] the unusual magnetic behavior of galvinoxyl has been observed as a function of solid solutions with **II**. The paramagnetic susceptibilities follow the Curie-Weiss law above the $T_{MAX}$ with the positive Weiss constants ($\theta$) ranging between +12 and +16 K. The low

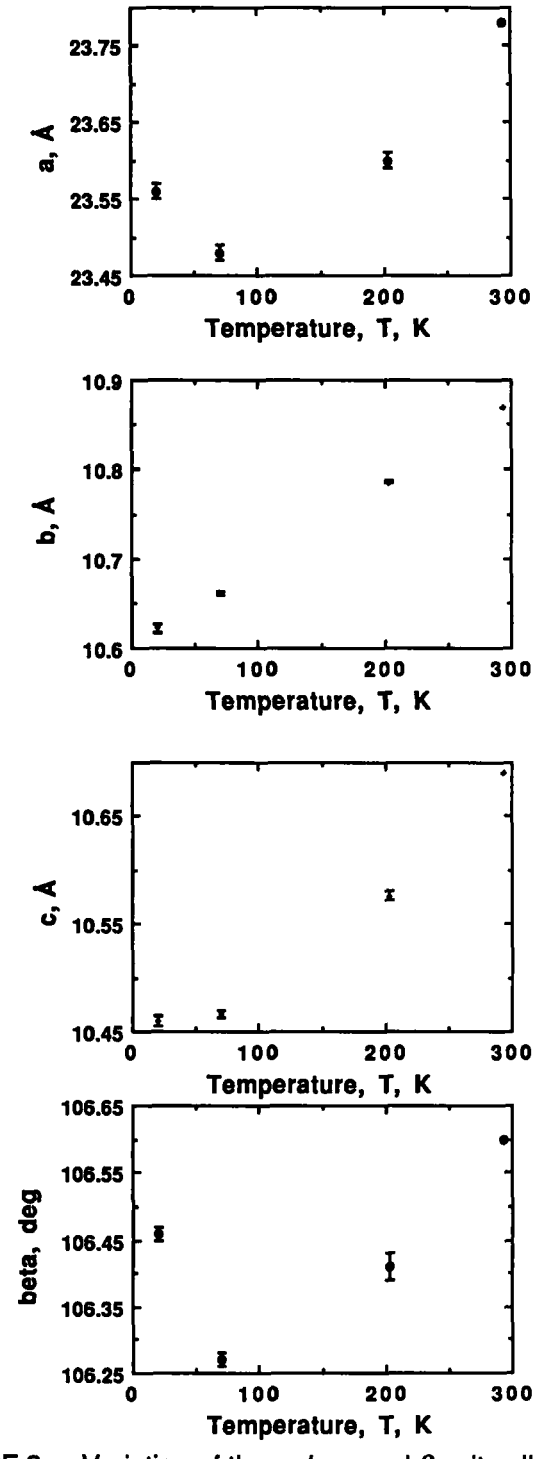



FIGURE 3 Variation of the *a*, *b*, *c*, and $\beta$ unit cell parameters with temperature for $[galvinoxyl]_x[hydrogalvinoxyl]_{1-x}$ (the room temperature data is taken from ref. 3)

radical concentration of commercial sample indicates the presence of a substantial amount of diamagnetic impurities; probably **II** from which **I** is prepared. As the temperature is lowered the magnetic susceptibility obeys the Curie-Weiss law and raises with temperature; however, it drops abruptly and at 76 K achieved a minimum value before it again increases. This incomplete phase transition is probably resulted from the contamination of hydrogalvinoxyl in the sample.

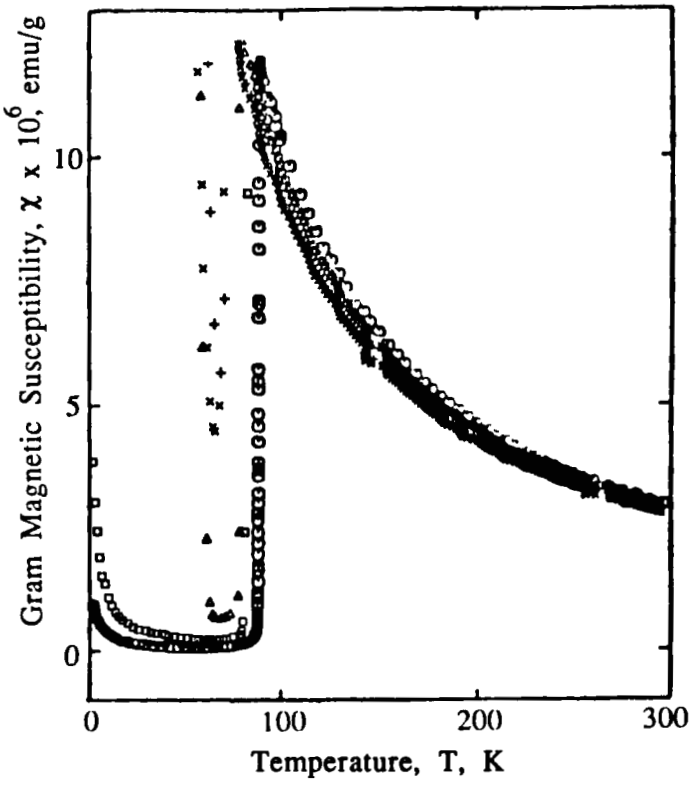



FIGURE 4 Gram Magnetic Susceptibility of Galvinoxyl vs Temperature: Aldrich sample (x), **A** (+), **B** (Δ), **C** (□), and from ref 1a (o).

TABLE 9 Magnetic Susceptibility Data of $[galvinoxyl]_x$-$[hydrogalvinoxyl]_{1-x}$ as a Function of Purification

| | C, emu K/mol | θ, K | % Radical | $T_{MAX}$, K |
|---|---|---|---|---|
| Aldrich | 0.337 | 15.2 | 90% | 74 |
| Sample **A** | 0.347 | 13.5 | 96% | 74 |
| Sample **B** | 0.365 | 12.6 | 98% | 81 |
| Sample **C** | 0.356 | 15.7 | 95% | 87 |

The susceptibility data is thus, directly compared to those reported for 4:1, 6:1, 9:1, and 19:1 galvinoxyl:hydrogalvinoxyl as well as 'pure' galvinoxyl,[1b] Fig. 5. The data taken on sample **A**, curve ***D***, sits midway between the data obtained for 6:1 and 9:1 galvinoxyl:hydrogalvinoxyl, we estimate the composition of our sample to be $[galvinoxyl]_x[hydrogalvinoxyl]_{1-x}$ ($x = 0.85 \pm 0.02$). **A** exhibited a similar magnetic behavior with a reduced susceptibility reduction below $T_{MAX}$ than the commercial sample. It is believed that recrystallization of galvinoxyl from acetonitrile, although leading to the isolation of large well-formed crystals, does not separate the hydrogalvinoxyl from the galvinoxyl.

The susceptibility of **B**, with the highest radical concentration, sharply dropped to a low value at 81 K, but started rising in value at 64 K. In comparison with the data reported by Kinoshita and coworkers[1b] **A** and **B** appear to be the mixed crystals of galvinoxyl/hydrogalvinoxyl with different amounts of hydrogalvinoxyl.

The hydrogavinoxyl-free sample, **C**, exhibited a dramatic drop in the paramagnetic susceptibility at 87 K which remained nearly diamagnetic down to very low temperature, Fig. 4. This result is in agreement with the previous report by Kinoshita and coworkers.[1a]

## CONCLUSION

The crystal structure of the solid solution of $[galvinoxyl]_x[hydrogalvinoxyl]_{1-x}$ ($x = 0.85 \pm 0.02$) has been determined at 20 and 203 K. No apparent change in the crystal structure was detected when the results of these structures are compared to each other and the earlier reported structure obtained at room temperature. Attempts to obtain the crystal structure of hydrogalvinoxyl-free sample, **C**, were unsuccessful due to disintegration of the crystals as the samples were cooled through $T_{MAX}$. This suggests a major transformation

occurs which leads to the loss of integrity of the crystal; thus, this mysterious phase transition remains unsolved.



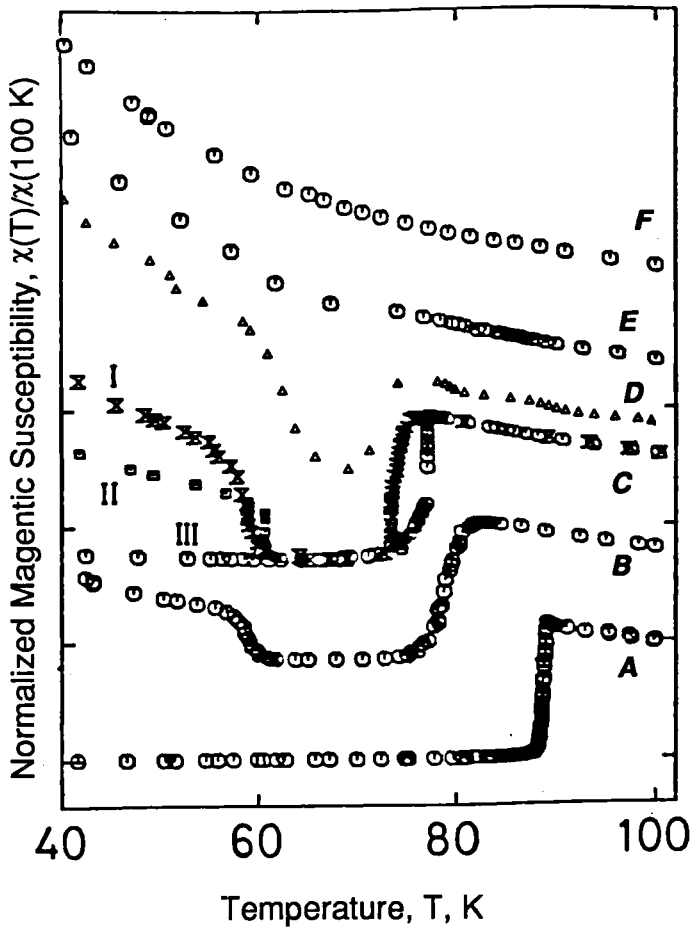



FIGURE 5 Molar Magnetic Susceptibility of Galvinoxyl between 40 and 100 K for $[galvinoxyl]_x[hydrogalvinoxyl]_{1-x}$ [x = 1 (*A*), 0.95 (*B*), 0.89 (*C*), 0.85 (*D*), 0.82 (*E*), 0.20 (*F*). Curves *A*, *B*, *C*, *E*, and *F* were taken from ref. 1b.

## ACKNOWLEDGMENT

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## REFERENCES

1. (a) K. Awaga, T. Sugano, and M. Kinoshita, *Solid State Commun. 57*, 458 (1986). (b) K. Awaga, T. Sugano, and M. Kinoshita, *J. Chem. Phys. 85*, 2211 (1986). (c) K. Awaga, T. Sugano, and M. Kinoshita, *Synth. Met. 27*, B631 (1988).
2. (a) K. Mukai, H. Nishiguchi, and Y. Deguchi, *J. Phys. Soc. Japan 23*, 125 (1967). (b) K. Mukai, *Bull. Chem. Soc. Japan 42*, 40 (1969).
3. D. E. Williams, *Mol. Phys. 16*, 145 (1969).
4. K.-M. Chi, J. C. Calabrese, and J. S. Miller, This proceedings
5. (a) The diamagnetic contribution of $-302 \times 10^{-6}$ emu/mol was calculated by the Pascal's method. (b) J. S. Miller, D. A. Dixon, J. C. Calabrese, C. Vazquez, P. J. Krusic, M. D. Ward, E. Wasserman, and R. L. Harlow, *J. Am. Chem. Soc. 111*, 0000 (1989).