# The Non-radical Nature of the Barium salts of Alloxantin, Tetramethyl-alloxantin and Hydrindantin. Studies in Magnetochemistry 10

R. W. ASMUSSEN and H. SOLING

The Chemical Laboratory B, Technical University of Denmark, Copenhagen, Denmark
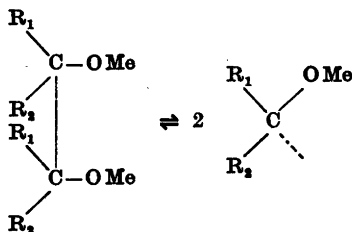
A magnetochemical investigation of the blue and blue-violet bariumsalts of alloxantin, tetramethyl-alloxantin and hydrindantin has proved that these compounds in contrast to the proposal of Hantzsch are not free radicals related to the metal-ketyls. The difference between the molar susceptibilities measured and calculated shows the existence of a small temperature-independent paramagnetism.

The barium salts of alloxantin, tetramethyl-alloxantin and hydrindantin are deep blue or blue-violet coloured and according to A. Hantzsch [1] rather instable towards oxygen and carbon dioxide. Hantzsch explained the halochromism of these compounds "durch die Bildung von dreiwertigem Kohlenstoff als wesentlichsten Bestandteil des chromophoren Komplexes der violetten Salze — also formell einfach durch Halbierung der aus den symmetrischen pinakon-ähnlichen Formeln der Alloxantine abzuleitenden Salzformeln".
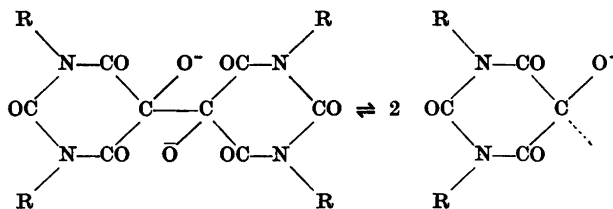
R=H, salt of alloxantin;   R=CH$_3$, salt of tetramethyl-alloxantin.

Hantzsch also points out that these salts are nearly related to the metal-ketyls of W. Schlenck [2]. The metal-ketyls may be considered as partly dissociated pinacolates:

$$R_1 \diagdown \text{C}-\text{O Me} \diagup R_2 \diagdown R_1 \diagdown \text{C}-\text{O Me} \diagup R_2 \quad \rightleftharpoons 2 \quad R_1 \diagdown \text{C} \diagdown \text{O Me} \diagup R_2$$

R₁ and R₂ equal or different aromatic radicals.

The normal state of the pinacolate molecule is a singlet state. The ketyl-form having one uncompensated electron is in a doublet state. The magnetic measurement gives directly the multiplicity of the molecule in the normal state in the crystal. In case of an equilibrium between the pinacolate molecule and the ketyl molecule it will be possible to calculate the degree of dissociation a of the pinacolate molecule by means of:

$$a = \frac{\chi_M}{2 \cdot 1\,270 \cdot 10^{-6}}$$

where χ_M is the observed molar magnetic susceptibility and $1\,270 \cdot 10^{-6}$ is the molar magnetic susceptibility of a molecule in a doublet state ("spin only" value).

Our first magnetic measurements gave at room temperature for the barium salt of alloxantin a molar magnetic susceptibility $= + 396 \cdot 10^{-6}$ (corrected for diamagnetism). This corresponds to an a-value of 15 %. We might then conclude that the interpretation of Hantzsch be correct. However, the measurements of further two different preparations of the bariumsalt of hydrindantin gave at room temperature diamagnetic susceptibilities of practically the same value. Furthermore our experiences concerning the stability of these compounds are in contrast to those of Hantzsch. After isolation from the mother liquor and drying are the salts rather stable. They may be kept unaltered for several days without protection. When suspended in water their colour will only fade very slowly when oxygen or carbon dioxide is passed through the suspension. The salts behave in these respects very differently from the metal-ketyls, which are highly sensible to moisture and oxygen. We then measured the magnetic susceptibilities of the barium salt of alloxantin and the two samples of the barium salt of hydrindantin at different values of the magnetic field strength (4 000—8 000 Ørsted). The results are given in Fig. 1, curve A₁ and H₁, respectively. The paramagnetism of the barium alloxantin salt originates in a ferromagnetic impurity, which also is present in the two samples of barium hydrindantin. The preparations of the salts were then repeated after having recrystallized the barium hydroxide 3 times (the salts themselves can not be recrystallized). These highly purified prepara-
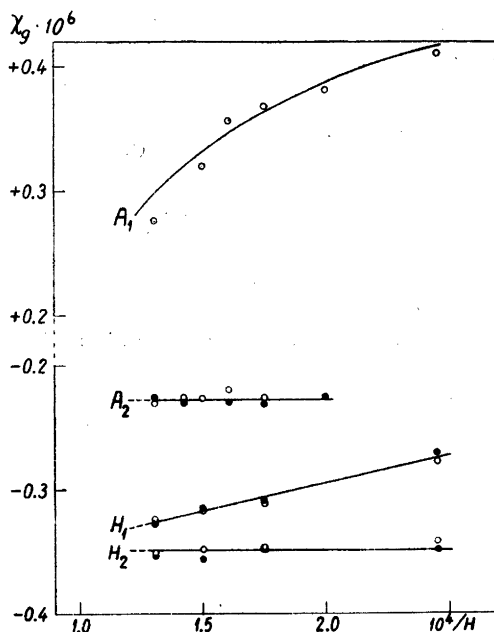
Fig. 1. *Magnetic susceptibilities per gram plotted against the reciprocal of the magnetic field strength. The curves A_2, H_1 and H_2 give the results for 2 different samples of barium alloxantin and barium hydrindantin (○ and ● respectively).*

tions were magnetically pure and the susceptibilities were all negative and independent of the magnetic field strength as shown in Fig. 1, curves A_2 and H_2. The magnetic susceptibilities of the barium salts of alloxantin, tetramethyl-alloxantin and hydrindantin are all negative and practically independent of the temperature in the interval: liquid-air temperatures to room temperature (Table 1). The organic components and the barium hydroxide used were also diamagnetic.

The difference between the measured molar susceptibilities of the barium salts and the molar susceptibilities calculated by means of Pascal and Pacaults increments (for Ba and H respectively —38.2 and —2.93) results in all cases in a small paramagnetic increment (Table 2). A similar small temperature-independent paramagnetism is well known in other deeply coloured compounds, which have a total molar magnetic susceptibility of negative value.

The barium salts here investigated do consequently not contain radicals and are not to be compared with the metal-ketyls. In the case of the metal-ketyls Eugen Müller and co-workers [3] have shown that the amount of free radical ranges from practically zero and to nearly 96 %, *e.g.* flavone potassium and Michler's ketone potassium respectively. The barium salts of alloxantin, tetramethyl-alloxantin and hydrindantin may be considered either as pinaco-lates or possibly as being derived from acetal like configurations. The magnetic method alone can not distinguish between these two possibilities.

EXPERIMENTAL

Magnetic measurements

We have applied the Gouy-method using a microbalance for the force determinations. The magnetic field strength may be varied from 4 000 to 8 000 Ørsted and the magnetic susceptibilities may be determined in the temperature interval 85 °K to 673 °K. The results of the measurements are given in Fig. 1, Table 1 (gram susceptibilities χ_g) and Table 2.

Table 1.

Substance	Sample No.	Analysis % Ba		$\chi_g \cdot 10^6$		
				295 °K	195 °K	85 °K
Barium alloxantin $C_8H_2O_8N_4Ba_2$	2	calc:	49.34			
		found:	51.41	— 0.225	— 0.232	—
	3	found:	49.36	— 0.228	— 0.259	— 0.279
Barium tetramethyl-alloxantin	1	calc.:	28.76			
		found:	29.50	— 0.320	— 0.354	— 0.341
$C_{12}H_{12}O_8N_4Ba$						
	4	found:	28.84	— 0.326	— 0.371	— 0.351
Barium hydrindantin $C_{18}H_8O_6Ba$	4	calc.:	30.02			
		found:	29.71	— 0.347	— 0.356	— 0.366
	5	found:	29.82	— 0.351	— 0.344	— 0.381

Table 2 gives the molar susceptibilities measured (χ_{exp}) and the calculated molar susceptibilities (χ_{calc}) above referred to. In the two cases where the preparation directly gives a dihydrate, these were also measured magnetically together with the anhydrides. The results are in good agreement.

Table 2.

Molar Susceptibilities Substance	$\chi_{exp} \cdot 10^6$	$\chi_{calc} \cdot 10^6$	$(\chi_{exp} - \chi_{calc}) \cdot 10^6$
Alloxantin dihydrate	— 130	— 128	— 2
Alloxantin	— 104	— 102	— 2
Barium alloxantin	— 126	— 168	+ 42
Tetramethyl-alloxantin	— 149	— 150	+ 1
Barium tetramethyl-alloxantin	— 155	— 181	+ 26
Hydrindantin dihydrate	— 169	— 179	+ 10
Hydrindantin	— 141	— 153	+ 12
Barium hydrindantin	— 160	— 174	+ 14

Preparation of the compounds

Alloxantin, tetramethyl-alloxantin and hydrindantin were prepared following literature methods of Nightingale [4], Biltz [5] and Ruhemann [6], respectively.

Ba(OH)$_2$ · 8H$_2$O was an ordinary c.p. product. This compound was purified by recrystallization 3 times. An aqueous solution (0.1 molar) was applied for the preparation of the barium salts. The hydroxide solution was refluxed for half an hour and filtered before use.

Barium alloxantin according to Hantzsch [1] by mixing a solution of alloxantin with the equivalent amount of a 0.1 M barium hydroxide solution.

Barium tetramethyl-alloxantin and *barium hydrindantin* were prepared by shaking the finely powdered organic component with a 5 % excess of a 0.1 M barium hydroxide solution for 4—5 hours.

The salts were in all cases collected on filter-crucibles, washed three times with ethanol then dried in vacuum. All preparations and packing of the powdered salts in the magnetic measuringtubes were undertaken in a nitrogen atmosphere. The tubes were evacuated and then sealed off.

Quantitative analysis. Barium was determined as barium sulphate (micro-method).

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