Inorganica Chimica Acta, 195 (1992) 131–132

Inorganica
Chimica Acta
LETTER

Diamagnetic susceptibilities of porphyrins

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(Received December 3, 1991)

Diamagnetic susceptibilities of metal-free porphyrin molecules are often needed to interpret the magnetic properties of metalloporphyrins, and such measurements have been published for only seven different compounds by four groups over the past thirty years [1–5]. We report the diamagnetic susceptibilities of fourteen common free-base porphyrins. Using Pascal's constants, the results for each derivative were used to predict the value for the parent molecule, porphin. Such predictions are found to be in excellent agreement with the result for porphin itself.

Experimental

The porphyrins were samples from previous [6, 7] studies. They were freshly purified on alumina or silica gel columns, or by thick layer TLC on silica gel plates, and then recrystallized. Absorption spectra gave no evidence of metal contamination and the compounds were dried under vacuum for 20 h at 150 °C.

The susceptibility measurements on ~30 mg samples under 600 torr of helium at 300 K were done on an updated version of a Cahn suspension Faraday balance used before on porphyrins [8–11] and geological [12, 13] samples. The balance was programmed to take magnet off–magnet on–magnet off readings at 5 s intervals, and the two 'off' readings are averaged and subtracted from the 'on' reading. This process is repeated, and the average of the two determinations is used to calculate a gram susceptibility point. Four points were automatically collected at each field, at four different fields between 2.1 and 3.4 kOe. Metallic platinum was used as the primary susceptibility standard.

Results and discussion

For each of the fourteen compounds investigated, the observed gram susceptibility, X_0, was a function of the applied field strength (H_a), and the same was noted before in related studies [2, 11] on porphyrins. This variation is attributed to trace ferromagnetic impurities.

TABLE 1. Diamagnetic susceptibilities of porphyrins, 300 K

Porphyrin[a]	Molar susceptibility ($-X_M \times 10^6$ cgs emu/mol)	
	Observed	Predicted for porphin
Porphin	311±45	311±45
H_2-TPP	481±3 700 (572)[b] 386[c]	278±2
H_2-OEP	450±6	259±4
H_2-T(Ethyl)P	422±12	327±9
H_2-ETIO-I	480±17	338±12
H_2-T(Propyl)P	427±17	284±31
H_2-TPyP(4)	427±46	252±10
H_2-Proto-IX-DME	492±19 509±15 585[d]	351±10
H_2-Deutero-IX-DME	411±4	252±2
H_2-Meso-IX-DME	461±15 595[d]	255±8
H_2-Monoester	544±10	394±7
H_2-T(4-i-PrP)P	702±18 853 (735)[b]	340±9
H_2-T(3-i-PrP)P	757±14	395±7
H_2-T(2-MeP)P	646±19 734 (620)[b]	382±11
H_2-T(4-MeP)P	731 (620)[b]	
H_2-PF	690[e]	

[a] Abbreviations: H_2-TPP is tetraphenylporphyrin; H_2-OEP is octaethylporphyrin; H_2-T(Ethyl)P is *meso* (5,10,15,20-) substituted (ms) tetraethylporphyrin; H_2-ETIO-I is etioporphyrin-I; H_2-T(Propyl)P is ms-tetrapropylporphyrin; H_2-TPyP(4) is ms-tetrakis(4-pyridyl)porphyrin; H_2-Proto, Meso and Deutero-IX-DME are the dimethylesters of proto, meso and deuteroporphyrin-IX; H_2-Monoester is the 1,4,6,7,8-pentamethyl-2,3-diethyl-5-acetic acid methylester porphyrin; H_2-T(4 and 3-i-PrP)P are the ms-tetrakis(4- and 3-isopropylphenyl)porphyrins and H_2-T(4-(or 3)-MeP)P are the ms-tetrakis(4-(or 3)-methyphenyl)porphyrins; H_2-PF is the tetra-alpha isomer of the ms-tetra(*o*-pivalamidophenyl)-porphyrin. [b] Data from ref. 2. The first value is the average of those extrapolated by eqn. (1), while that in parentheses is the average of the 'average' values reported. [c] Ref. 3. [d] Ref. 4. [e] Ref. 5. This value extrapolates (ref. 2) to -467×10^{-6} for H_2-TPP.

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0020-1693/92/$5.00

At applied fields of less than 6 kOe, the Honda–Owen [14] equation is of the form

$$X_0 = X_d + \sigma/H_a \tag{1}$$

where X_d is the gram diamagnetic susceptibility and σ the ferromagnetic saturation magnetization. Plots of X_0 versus $(1/H_a)$ are linear for H_a values between 2.1 and 3.4 kOe, and the least-squares determined intercept at $(1/H_a) = 0$ gives X_d. Based on the observed σ values, and with a σ of 218/g for metallic [15] iron, 1–10 ppm of ferromagnetic iron as the impurity can account for the dependence of X_0 on H_a for these derivatives. Table 1 is a list of the molar diamagnetic susceptibilities (X_M) for the fourteen porphyrins studied, along with data from other investigators. Pascal's constants [15] were used to predict for each porphyrin a susceptibility for the unsubstituted porphyrin, porphin.

Our susceptibilities are in reasonable agreement with those found earlier on the same porphyrins by other workers (Table 1), and are closer to the 'average' values reported by Eaton and Eaton [2] than their extrapolated (eqn. (1)) results. For thirteen porphyrins which include both *meso* and beta pyrrole substituted derivatives, the average predicted for porphin is $(-316 \pm 55) \times 10^{-6}$ cgs emu/mol. This is in the range of $(-311 \pm 45) \times 10^{-6}$ cgs emu/mol found for porphin itself. In conclusion, the diamagnetic susceptibilities of free-base porphyrins can be calculated with some confidence by application of Pascal's substituent constants to the diamagnetic susceptibility found for the basic porphyrin molecule, porphin.

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