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Comment of the Use of $HgCo(NCS)_4$ as Susceptibility Standard

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Introduction

Magnetic susceptibility measurements are of interest to inorganic chemists since they allow the calculation of magnetic moments and thus give information on the electronic structure of complexes. Many reported measurements are performed using $HgCo(NCS)_4$ as susceptibility standard [1], as proposed by Figgis and Nyholm who first measured its mass susceptibility at 20 °C ($16.44 \pm 0.08 \times 10^{-6}$ cgsu) and who gave an evaluation of its Weiss temperature ($\theta = -10$ K) [2]. Since then, three other Curie–Weiss parameter sets have been proposed for $HgCo(NCS)_4$ [3–5]. This, combined with misinterpretation of earlier work and with other confusion, results in a rather complicated situation for the experimental chemist who wants to calibrate a magnetic susceptibility apparatus in the 80–300 K temperature range.

The experimentally observed susceptibility of a given material results from the addition of a temperature dependent paramagnetic susceptibility (>0) and of a temperature independent term due to diamagnetic susceptibility (<0):

$$\chi_{obs} = \chi_{para} + \chi_{dia} \tag{1}$$

The Curie–Weiss law expresses the temperature dependence of the molar paramagnetic susceptibility:

$$\chi_{M,para}(T) = C/(T - \theta) \tag{2}$$

Combining (1) and (2) gives the following expression for the mass susceptibility:

$$\chi_{m,obs}(T) = \frac{C/(T - \theta) + \chi_{M,dia}}{MW} \tag{3}$$

C and θ can thus be determined from the experimental data by calculating the straight line:

$$1/(MW \cdot \chi_{m,obs}(T) - \chi_{M,dia}) = T/C - \theta/C \tag{4}$$

Discussion

The available data are summarized in Table I. The mass susceptibility of $HgCo(NCS)_4$ at 20 °C is well established, the two experimentally determined values being in excellent agreement. Moreover, it is clear that 16.44×10^{-6} cgsu represents the total (uncorrected) susceptibility, contrary to the suggestion of Hatfield *et al.* [4]. The confusion arises from a discrepancy between two papers by Figgis and Nyholm [2, 6] which has long been pointed out by Cotton *et al.* [7].

Räde [3] does not specify which diamagnetic correction he uses to obtain $\theta = 2$. Fitting his data into (4) however leads to $C = 2.433 \pm 0.041$, and $\theta = 2.4 \pm 2.3$ when a molar diamagnetic correction of -189×10^{-6} cgsu (*vide infra*) is used; the correlation coefficient (CC) is 0.99929. Hatfield *et al.* use no diamagnetic correction, fitting a straight line through experimental data which do not obey a linear law. These authors show, however, that $HgCo(NCS)_4$ is not a perfect paramagnet and that it is not expected to follow exactly the Curie–Weiss law anyway. Nevertheless, the mass susceptibility they deduce from the calculated C and θ parameters is 1.5% smaller than the experimental value at 20 °C;

TABLE I. Curie–Weiss Parameters and χ_m (293.16) for $HgCo(NCS)_4$.

Temperature Range (K)	Method	$10^6 \cdot \chi_m$ (293.16) (cgsu)	$10^6 \cdot \chi_{M,dia}$ (cgsu)	C	θ (K)	Reference
80–300	Gouy	16.44 ± 0.08[a]	−137		−10[b]	2
5.8–293	Faraday	16.45 ± 0.10[a]	[c]		+2[d]	3
1.7–50	Faraday + vibrometer	16.20[e]	[f]	2.351 ± 0.002	−1.86 ± 0.01	4
1.3–102.6	Faraday + vibrometer	16.39[e]	−141.8	2.41	−0.62	5

[a] Experimental value. [b] The authors report +10 and use T + θ in the Curie–Weiss law. [c] Not specified. [d] A revised value of −1.8 has been proposed, *cf.* [4]. [e] Extrapolated value using the C and θ parameters. [f] No correction applied to calculate C and θ; the authors propose -190×10^{-6} cgsu.

this result is excellent considering the 240° extrapolation, but it is not satisfying for a calibration standard. The data of O'Connor *et al.* [5] yield more precise parameters for extrapolation into the high temperature range and a calculated susceptibility of 16.39×10^{-6} cgsu (and not 16.50 as stated in [5]). We have fitted their data into (4) and we were not able to reproduce the θ value; we find: $C = 2.41 \pm 0.01$, $\theta = -1.0 \pm 0.2$, $CC = 0.99972$, which gives $\chi_m\ (293.16) = 16.27 \times 10^{-6}$ cgsu. The same fit performed without diamagnetic correction, as recommended in [4], yields $C = 2.40$, $\theta = -0.95$, and $CC = 0.99969$. Since CC is slightly better when a diamagnetic correction is applied, we decided to look more precisely which correction should be used. According to [8], the following ionic corrections apply: -37, -12, and -35×10^{-6} cgsu/at.-g for Hg(II), Co(II), and NCS^-, respectively. The molar diamagnetic correction for $HgCo(NCS)_4$ amounts then to -189×10^{-6} cgsu, a value practically identical with the one proposed in [4]. The correction of -141.8×10^{-6} cgsu used by O'Connor *et al.* arises from the use of atomic, and not ionic, correction for Hg and Co. Using a diamagnetic correction of -189×10^{-6} cgsu with O'Connor's data yields $C = 2.42 \pm 0.01$, $\theta = -1.1 \pm 0.2$, $CC = 0.99976$, and $\chi_m\ (293.16) = 16.34 \times 10^{-6}$ cgsu. We were not able to extract the diamagnetic correction from a fit of the experimental data to equation (3): the non-linear least-square procedure did not converge properly.

Conclusion

Under 100 K, recommendation of Hatfield *et al.* to choose a copper complex as susceptibility standard should be followed [4]. For higher temperatures, $HgCo(NCS)_4$ remains an acceptable standard. We think equation (3) should be used, with a molar diamagnetic correction of -189×10^{-6} cgsu. The Weiss temperature should be evaluated from low temperature data, but the C parameter should be calculated using experimental data which extend over a much larger temperature range. We recommend the following values: $C = 2.433$ and $\theta = -1.1$, which lead to $\chi_m\ (293.16) = 16.43 \times 10^{-6}$ cgsu.

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