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Short Communication

Magnetic Properties of Group VI B Hexacarbonyls. Suggestion of a New Diamagnetic Susceptibility Standard

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Summary. Careful measurements of the magnetic susceptibilities of group VI B metal hexacarbonyls show an ideal diamagnetic behaviour. The properties of $W(CO)_6$, together with the relatively low price, lead to the suggestion of $W(CO)_6$ as a new calibration standard for the diamagnetic region.

Keywords. Metal hexacarbonyls; Magnetic susceptibility; Diamagnetism.

Magnetische Eigenschaften von Hexacarbonylen der Gruppe VI B.
Vorschlag zu einem neuen diamagnetischen Suszeptibilitätsstandard

Zusammenfassung. Sorgfältige Messungen der magnetischen Suszeptibilität der Metallhexacarbonyle der Gruppe VI B zeigen deren ideal diamagnetisches Verhalten. Die physikalischen Eigenschaften des $W(CO)_6$, zusammen mit dem relativ niedrigen Preis, prädestinieren es als diamagnetischen Eichstandard.

Recently we performed a careful magnetic study on the group VI B carbonyls $M(CO)_6$ with M = Cr, Mo, W in pure and mixed crystals. In the course of this work the availability of reliable diamagnetic calibration standards became important. The usual diamagnetic standard, KCl (e.g., Merck suprapur), is very expensive and there is always some risk for contaminations with paramagnetic impurities. Therefore, the search for alternative substances is desirable which are both relatively inexpensive and easy to purify.

The group VI B hexacarbonyls, $M(CO)_6$, are colourless, stable crystalline materials which are easily purified due to their relatively low sublimation temperatures [about 380 K, 420 K and 425 K under a low pressure of ca. $2.5 \cdot 10^3$ Pa for $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$, respectively]. The $M(CO)_6$ polyhedra show almost ideal octahedral structure [1–3]. The formal oxidation state 0 of the metal together with the carbonyl ligand point at ideal diamagnetic behaviour.

With the exception of a work by Klemm et al. [4] no data concerning the magnetic susceptibilities of the group VI B hexacarbonyls were reported to our knowledge.

Our values of the mass susceptibility (given in $m^3\,kg^{-1}$) are $-5.04 \cdot 10^{-9}$, $-5.18 \cdot 10^{-9}$ and $-4.40 \cdot 10^{-9}$ for M = Cr, Mo and W, respectively. These values correspond to the respective molar susceptibilities (in $m^3 mol^{-1}$) of $-1.11 \cdot 10^{-9}$, $-1.37 \cdot 10^{-9}$ and $-1.55 \cdot 10^{-9}$. The susceptibility values are reproducible to about $\pm 2\%$.

The investigation of the three binary mixed crystal systems and the ternary mixed crystal system showed a complete additivity of the magnetic susceptibilities. The correct mass susceptibility values of the mixed crystals were obtained simply by multiplying the individual mass susceptibilities with the molar fractions and summing up. In the Cr-rich compounds small deviations (ca. 2%) from the calculated value occurred. However, XRF-analysis showed a corresponding deviation in the composition of the mixed crystals from the starting mixture. This effect is due to the relatively high volatility of the $Cr(CO)_6$.

The careful evaluation of all our magnetic data classified $W(CO)_6$ as a calibration standard for the diamagnetic region. The compound has a relatively high density and an appropriate suceptibility value such that it fits best to the demand of a minimum sample volume using the Faraday technique.

Experimental

The magnetic susceptibility measurements were performed with the modified Faraday balance SUS 10 (manufactured by A. Paar KG in Graz, Austria) between 77 K and 350 K. The magnetic flux densities ranged from 0.4 T to 1.3 T. Calibration followed common literature procedures, using KCl [5] and $Hg[Co(NCS)_4]$ [6] as standard for the diamagnetic and the paramagnetic region, respectively. The carbonyls (Ventron) were purified by double sublimation in a simple home built sublimation apparatus; mixed crystals were obtained by thoroughly grinding together the pure carbonyls in the desired amounts and slow sublimation at about 325 K [7]. Due to the relatively high volatility and the possible health risk the sublimation should be performed in a fume hood.

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