Evidence for the Diamagnetism of $Co(NO)_2Hal.$ and $Fe(NO)_2Hal.$

Studies in Magnetochemistry 20 *

H. SOLING and R. W. ASMUSSEN

The Chemical Laboratory B, Technical University of Denmark, Copenhagen, Denmark

The magnetic susceptibilities of $Co(NO)_2X$, X = I, Br, Cl, and $Fe(NO)_2Y$, Y = I, Br, have been measured at temperatures ranging from 85 to 295°K. The compounds are found to be diamagnetic or nearly so. This result is compatible with the generally accepted binuclear structures, if in the particular case of the iron compounds an intermetallic bond be supposed. The preparation and the purification of the compounds are described in detail.

In the years 1939 and 40 Hieber and coworkers [1,2] prepared a series of metal-NO-halides of the composition $Co(NO)_2X$ and $Fe(NO)_2Y$, where X = I, Br, Cl and Y = I, Br. All the compounds are very instable, black solids with low melting points. They can be prepared by the action of NO-gas on the appropriate anhydrous metal-di-halide eventually under addition of metal powder, *e.g.*

$$FeI_2 + Fe + 4NO \rightarrow 2Fe(NO)_2I$$
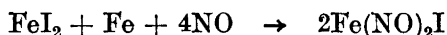
In the present paper a magnetochemical investigation of the above mentioned compounds is reported.

The results of the measurements of the magnetic susceptibility of several samples of $Co(NO)_2I$, $Co(NO)_2Br$, $Co(NO)_2Cl$ and $Fe(NO)_2I$ are given in Table 1 together with the results of the chemical analyses of the compounds. The independent samples Nos. I to V of $Co(NO)_2I$ have been prepared by consecutive sublimations of the crude product. Considering the measurements at room temperature it is seen that the gram susceptibility decreases from No. I to No. IV; the difference between Nos. IV and V is considered of no significance. (*Cf.* the remarks below concerning the accuracy of the measurements). The low-temperature measurements of the samples No. I to No. IV display the

---

* No. 19 of this series: *Acta Chem. Scand.* **11** (1957) 1435.

Table 1. Analyses and magnetic gram susceptibilities of the compounds $Me(NO)_2Hal$

Compound		Analyses % Metal	% Halg	$\chi_g \cdot 10^6$ at 295°K	$\chi_g \cdot 10^6$ at 195°K	$\chi_g \cdot 10^6$ at 85°K
$Co(NO)_2I$	calc.	23.97	51.61			
No. I	found	24.05	51.24	0.173	0.309	0.85
No. II	»	23.89	51.55	−0.017	0.018	0.39
No. III	»	24.09	51.65	−0.034	−0.017	0.19
No. IV	»	24.04	51.47	−0.105	−0.109	−0.01
No. V	»		51.40	−0.108		
$Co(NO)_2Br$	calc.	29.64	40.18			
No. I	found	29.77	40.09	0.023		
No. II	»	29.63	40.20	−0.027		
$Co(NO)_2Cl$	calc.	38.17	22.96			
No. I	found	38.36	22.96	0.076		
No. II	»	38.12	22.88	0.025		
$Fe(NO)_2I$	calc.	23.00	52.28			
No. I	found	23.08	52.21	−0.142	−0.143	−0.18
No. II	»	22.96	52.05	−0.139	−0.149	−0.16

same features. On the other hand, when considering each preparation separately χ_g increases when the temperature is decreased. The absolute increase is the largest for preparate No. I, which has a positive susceptibility. Remembering that $Co(NO)_2$ I is undergoing some decomposition when exposed to the air even for a short time and that the products of decomposition must be strongly paramagnetic or even ferromagnetic, it seems safe to conclude that chemically pure $Co(NO)_2$ I is diamagnetic. The good accordance between the analysed and the calculated composition of the substances rather strengthens than weakens this conclusion since the amount of an ordinary paramagnetic cobaltous-compound necessary to mask completely even a strong diamagnetism is beyond the limits of what can be found by a chemical analysis.

In the cases of $Co(NO)_2Br$ and $Co(NO)_2Cl$ magnetic measurements have been performed at room temperature only. A faint diamagnetism was ultimately found for the bromide while an equally small paramagnetism was the best result we could reach with the chloride. These two compounds are even more liable to undergo decomposition than the iodide. It is furthermore highly improbable that the magnetic properties of the bromide and the chloride should be essentially different from that of the iodide. We consequently conclude that also $Co(NO)_2Br$ and $Co(NO)_2Cl$ are diamagnetic when chemically pure.

$Fe(NO)_2I$ is the only substance for which we found a reproducible, although very small, diamagnetism independent of the temperature. The apparently increased diamagnetism at lower temperatures is not considered significant. Usually we claim a much higher accuracy, but remembering that the magnetic susceptibility is found from the difference between the force exerted by the magnetic field upon the Gouy-tube + substance and that exerted upon the
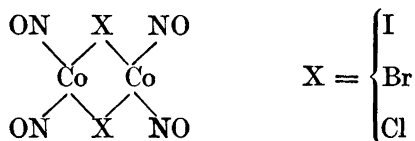
Table 2. Magnetic gram susceptibilities of $Fe(NO)_2I$ at different temperatures and different field strengths.

Temperature, °K	295		195		85	
Field Strength, Ørsted	6 226	7 636	3 346	4 194	3 346	4 194
Force (in mg) exerted on: a: Container + Sample b: Container	1.238 0.894	1.890 1.363	0.364 0.261	0.567 0.409	0.622 0.452	0.732 0.549
c: Sample	0.344	0.527	0.103	0.158	0.170	0.183
$-\chi_g \times 10^6$	0.139	0.144	0.145	0.141	0.183	0.170

empty tube, it is obvious that the experimental error must be rather large when so small susceptibilities are measured as the case is here. Furthermore, during the measurements at low temperatures a continuous condensation of ice upon the tube occurs, which considerably augments the experimental errors. As an illustration of these effects a series of measurements on $Fe(NO)_2I$ is shown in Table 2.

Besides the compounds listed in Table 1 we also prepared $Fe(NO)_2Br$ and attempted to measure it magnetically. In spite of several efforts shortly reported in the experimental section we did not succeed in obtaining even a qualitative impression of its susceptibility. We suppose, by extrapolation from the above results, that this compound is so instable that an experimental demonstration of its — presumed — diamagnetism is impossible.

Hieber and coworkers [1,2] have proposed a binuclear formula for the cobalt-compounds:

$$\begin{matrix} ON & X & NO \\ & \diagdown\diagup\diagdown\diagup & \\ & Co \quad Co & \\ & \diagup\diagdown\diagup\diagdown & \\ ON & X & NO \end{matrix} \qquad X = \begin{cases} I \\ Br \\ Cl \end{cases}$$

The NO-metal bond contributes, according to the detailed discussion given by Seel [3], three electrons to the electron system of the acceptor metal. The four-coordinated Co-atom thus obtains an EAN = 36 which accounts for the dia-magnetism. However, it must be pointed out, that since the monomer also contains an even number of electrons the above formula is no necessary consequence of the observed diamagnetism.

The four ligands around each Co-atom may utilize either the tetrahedral sp^3-hybrid or the planar dsp^2-hybrid. The latter necessitates the promotion of two electrons from the 3d orbitals to the 4p orbital not participating in the hybridization, and is therefore considered energetically less favourable.

$Fe(NO)_2Y$ contains an uneven number of electrons in the monomer form. A binuclear structure analogous to that shown above for the cobalt-compounds leaves one unpaired electron on each iron atom. The assumption of a high-

polymer structure is not in accordance with the low melting points and the fact that the compounds are easily sublimed. We consider a binuclear structure with an intermetallic bond the most acceptable explanation of the diamagnetism.

EXPERIMENTAL

Preparation and analysis of the compounds

The preparation of the compounds was carried out according to the method given by Hieber *et al.* [1,2] We have modified the technique in order to prepare the compounds in the highest possible degree of magnetic purity, and for the reason of easy handling the samples used for the magnetic measurements.

Co(NO)₂I. 4 g of powdered anhydrous CoI_2 were introduced in the apparatus shown in Fig. 1 and dried at 110—120°C in a current of dry nitrogen. After cooling to room temperature the nitrogen was displaced by pure, dry NO and the temperature slowly raised. At 60—80°C the powder began to react with the NO-gas under liberation of iodine which was collected on the "cold finger". When the reaction began to slow down, the temperature was cautiously raised to 105°C. The reaction vessel was maintained at this temperature until the evolution of iodine ceased. The apparatus was then cooled to room temperature. While a current of dry nitrogen was passed through, the "cold finger" was withdrawn, cleaned, dried and inserted again. The pressure was then reduced to about 1 mm Hg and the sublimation of $Co(NO)_2I$ was started by heating the apparatus to 80°C as quickly as possible. In the course of 5 to 6 h a brush of black crystals was collected on the "cold finger". This crude sublimate must be stored in an evacuated vessel. The purification of the product was accomplished by several resublimations.

Co(NO)₂Br was prepared analogously from an intimate mixture of powdered, anhydrous $CoBr_2$ and freshly reduced cobalt powder (from cobaltous-oxalate). The reaction started at 100°C. $Co(NO)_2Br$ forms black crystals.

Co(NO)₂Cl was obtained from anhydrous $CoCl_2$ and cobalt powder just as the corresponding bromide. Black crystals.
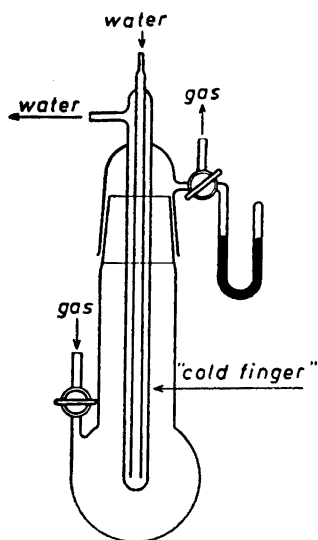

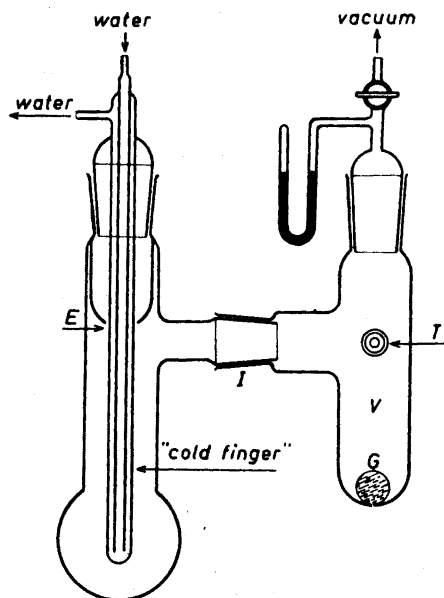*Fig. 1.* Reaction- and sublimation-apparatus.

Fig. 2. Sublimation apparatus with vessel (*V*), where the sublimate is powdered by means of the glass-sphere (*G*), and filled into the Gouy-tube (*T*). The edge (*E*) scratches the sublimate off the "cold finger".

While $Co(NO)_2I$ could be sublimed nearly without decomposition, the bromide and the chloride underwent a slight decomposition during the sublimation. All three substances are very sensitive to oxygen.

The *anhydrous cobaltous-halides* used were prepared from Ni-free $CoCO_3$ which was dissolved in the appropriate halogen acid. The solution was then evaporated to dryness under dropwise addition of acid to prevent hydrolysis. $CoCl_2$ was finally dried in a current of dry HCl at 120°C, while $CoBr_2$ and CoI_2 were dried at $130-140°C$ *in vacuo*. The substances were all completely soluble in water.

Fe(NO)₂I. 4 g of powdered anhydrous FeI_2 thoroughly mixed with 1 g of freshly reduced iron powder were treated with NO-gas as described above. The reaction started at room temperature under evolution of a considerable amount of heat, and was allowed to continue without further heating. From time to time slight cooling was necessary in order to keep the reaction under control. When the temperature exceeded 80°C the reaction mixture began to melt. No free iodine was observed during the reaction. The crude nitrosate was sublimed at $80-90°C$ under reduced pressure. In order to obtain a sublimate of a crystal size suitable for the further manipulations, the sublimation had to be carried out in three stages: *i*, 80°C, 10 mm Hg; the substance melted and gave off NO rather vigorously. *ii*, When the evolution of NO ceased, the temperature was raised to 85°C and the pressure was reduced to 5 mm Hg. The majority of the substance was volatilized at this stage. *iii*, Finally the temperature was raised to 90°C and the pressure was lowered to about 1 mm Hg. The sublimation was now continued until only a small remanence of iron powder and decomposed substance was left. The resublimations were carried out in the same way. No liberation of NO was then observed and the yield was nearly quantitative. $Fe(NO)_2I$ forms black crystals, sensitive to oxygen.

Fe(NO)₂Br was prepared in the same way as the iodide. This substance, which also forms black crystals, is the most delicate of the compounds described here. Like the

iodide' it sublimes easily, but far from quantitatively. $Fe(NO)_2I$, on the other hand, is the most stable of the five substances in question. A specimen of this substance stored in an evacuated glass-tube for three years did not show any sign of decomposition, while the other substances were more or less decomposed.

The *anhydrous ferrous-halides* used were prepared from iron powder and elementary halogens, according to standard procedures, and finally sublimed in high vacuum.

Analysis. Cobalt-compounds: Cobalt was determined as $CoSO_4$ by weighing. The compounds were converted into the sulphate, which was heated at 500°C until constant weight. Owing to the small amounts of substance available at that stage of development of the preparation technique the usual method of determination of iodine as AgI by weighing could not be used. The iodine was therefore oxidized to IO_3^- and determined iodometrically. Bromine and chlorine were weighed as the silver-halides.

$Fe(NO)_2I$: Iron was determined as Fe_2O_3 and the iodine as AgI. The results of the analyses are given in Table 1 together with the results of the magnetic measurements.

Magnetic measurements

The magnetic susceptibilities were measured by means of the Gouy method as described in earlier papers [4]. The susceptibility quoted for each sample and temperature in Table 1 is the mean value of several measurements at at least two field strengths ranging from 3 346 to 7 636 Ørsted (*cf.* Table 2). No sign of field strength dependence of the susceptibilities was found within the limits of experimental errors. In view of the obvious risk of ferromagnetic impurities in the preparates, measurements of the susceptibilities over a broader range of field strengths would have been desirable, but owing to the very feeble magnetism observed, the measurements could only be carried out with a reasonable accuracy (a few per cent) in the above mentioned interval of field strengths, 7 636 Ørsted being the maximum field strength obtainable with our magnet. On the other hand, a slight ferromagnetism would not invalidate our conclusion that the pure compounds are diamagnetic.

The delicacy of the compounds to oxygen complicated the packing of the substance into the tubes used for the magnetic measurements. The following procedure, which is the final result of several attempts, fulfils the demands for simplicity and efficiency to a reasonable degree. The resublimations were carried out in the apparatus shown in Fig. 2 as described above. After cooling to room temperature, the apparatus was tilted and while a current of dry nitrogen was passed through, the "cold finger" was slowly drawn out with a screwing movement. When reaching the edge *E* the crystals were scratched off and fell down into the vessel *V*, which then was disconnected at *J* and closed with a ground stopper. The vessel was evacuated, the crystals were powdered by aid of the glass-sphere *G* and could now be packed into the tube *T* by aid of a little glass rod (not shown in Fig. 2) containing an iron core, so that it could be manipulated from outside by means of a magnet. However, great difficulties were experienced at this point due to adhesion of the fine powder to the glass walls. We were therefore forced to abandon the fine-powdering and instead adapted the following way of packing. The crystals were only crushed coarsely with the glass-sphere and next filled into the tube in small portions. Each time the tube was tapped gently at the bottom until the packing appeared uniform by inspection with a magnifying glass. From our general experience concerning the packing of Gouy-tubes this procedure is judged to be sufficiently reproducible for the purpose, provided the size of the particles is nearly uniform and not too large. The apparatus was again connected to the vacuum-pump and the tube *T* was sealed off, while the pump was working. During the sealing-off process the upper surface of the packing melts slightly and locks the packing when it again solidifies, thus securing a defined length of the substance column. Since the upper surface of the packing is situated well outside the magnetic field during the measurements an eventual slight decomposition due to the melting cannot commit the measurements.

Several samples of $Fe(NO)_2Br$ were prepared as described above and measured magnetically. Rather large positive and completely irreproducible susceptibilities were found. Assuming that the crushing of the crystals might cause some decomposition, we finally filled the sublimate into the Gouy-tube without any crushing at all. Of course the packing became highly imperfect in this way, but still we might obtain some qualitative inform-

ation about the susceptibility. The glass-tube with the crystals was, however, still attracted by the magnetic field, and the attraction slightly increased with time. This clearly shows, that the substance is steadily decomposed even in the sealed-off tube. We therefore gave up further investigations of the magnetic properties of $Fe(NO)_2Br$.

REFERENCES

1. Hieber, W. and Marin, R. Z. anorg. allgem. Chem. **240** (1939) 241.
2. Hieber, W. and Nast, R. Z. anorg. allgem. Chem. **244** (1940) 23.
3. Seel, F. Z. anorg. allgem. Chem. **249** (1942) 308.
4. Asmussen, R. W. and Soling, H. Acta Chem. Scand. **8** (1954) 558, 563.