JOURNAL OF SOLID STATE CHEMISTRY 15, 292–296 (1975)

Magnetic Susceptibility of the One-Dimensional Conductor $(H_3O)_{1.6}$-$[Pt(C_2O_4)_2]nH_2O$

D. HEITKAMP, H. S. RÄDE,

Institut für Chemie, Kernforschungsanlage Jülich

H. J. KELLER, AND H. H. RUPP

Institut für Anorganische Chemie der Universität Heidelberg

Received March 3, 1975

The magnetic susceptibility of the dioxalatoplatinate acid $(H_3O)_{1.6}[Pt(C_2O_4)_2]nH_2O$, a mixed valency planar (MVP) compound with columnar structure and one-dimensional metallic conduction properties, has been measured in the temperature range 1.5–300°K. The observed paramagnetism, like in other MVP compounds, may be described by a linear $1/T$ dependence with a break in the slope at a characteristic temperature. The Curie constants as well as the point of discontinuity have been found to depend on the crystal water content. The results are discussed in terms of different theoretical concepts.

Introduction

Partially oxidized dioxalatoplatinate acid, $(H_3O)_{1.6}[Pt(C_2O_4)_2]nH_2O$, belongs to the class of mixed valency planar (MVP) transition metal complexes which, under certain conditions, exhibit one-dimensional metallic properties in the crystallized state. Much attention has been focused on these compounds in recent years (*1*, *2*).

Square planar complexes are formed mainly by transition metal ions with a d^8 electron configuration. X-ray investigations of crystallized planar complexes of this kind show that they stack face to face forming columnar compounds with direct metal–metal bonds between the complex forming metal ions (*3*). Due to a completely filled d^8-band these compounds are in general wide-gap semiconductors. However, if part of the electrons in the top filled band are removed by partial oxidation thereby producing metal ions of mixed valencies, one-dimensional metallic conductivity along the metal chains is observed in some cases. In the partially oxidized compounds the metal–metal distance is not very much larger than in the corresponding bulk metal. In $(H_3O)_{1.6}[Pt(C_2O_4)_2]nH_2O$ the Pt–Pt distance is 2.80 or 2.82 Å (for $n = 2$ or 3, respectively) compared to 2.77 Å in Pt-metal (*3*); the mean oxidation number of the Pt ions is 2.4.

An unusual magnetic behavior has been reported for a typical MVP compound. The magnetic susceptibility of $K_2[Pt(CN)_4]Br_{0.3}$-$3H_2O$ (KCP) (*4*) follows a nonuniform Curie law between 4°K and room temperature. There is a characteristic temperature dividing the temperature range into two zones where different Curie constants apply. This behavior also has been reported for iridiumcarbonylchloride (*5*). In this compound we have strong Ir–Ir interactions and one-dimensional metallic properties. However, it is not quite clear whether it may be classified a mixed valency chain compound (*6*). The origin of the discontinuity of the slope in the $1/T$ diagram (40°K for KCP and 25°K for iridium-

Printed in Great Britain

carbonylchloride) is hitherto unknown. The explanations given range from Pauli and Van Vleck paramagnetism to paramagnetic impurities and ordering of ions in the crystal upon a temperature change. Further experimental work is necessary to obtain a better understanding of the observed peculiar magnetic behavior. To investigate the question whether or not these properties are typical for MVP compounds, we measured the magnetic susceptibility of partially oxidized and unoxidized dioxalatoplatinate complexes in the temperature range from 1.5 to 300°K.

Experimental

The static magnetic susceptibilities were determined using the Faraday method. The apparatus consisted of a zero type balance which compensates the force exerted by the magnetic field keeping the sample always in the same position. Its resolution was 1 μg. The applied magnetic field amounted to 7000 Oe and was controlled by a Hall probe. The specimens were placed in a quartz container and suspended from the balance by a thin silver chain. The magnetic susceptibility of the empty system was constant over the whole temperature range. The system was calibrated by using the known susceptibility of $HgCo(SCN)_4$ which is 16.44×10^{-6} emu/g at 20°C (*7*). The temperature of the specimen was determined by means of a Ge-resistor in the low-temperature range (1.5–30°K) and a Au (+0.03% Fe)-alumel thermocouple for temperatures between 10 and 300°K.

The partially oxidized dioxalatoplatinate complex $(H_3O)_{1.6}[Pt(C_2O_4)_2]nH_2O$ was synthesized in a chemical procedure first described by Wahl (*8, procedure 1c*). Since the magnetic susceptibility of this compound was found to vary strongly with the quantity *n*, we had to make sure that the samples had a defined (though unknown) content of crystal water. Therefore, samples of the synthesized product were introduced into a precooled cryostat and rapidly cooled down to 77°K under atmospheric pressure of helium. Then the sample space was evacuated and filled with dry helium (pressure 0.1 Torr) which served as contact gas. The constancy of their weight prior to and after the evacuation process was taken to be an indication that these samples retained their original crystal water content. This is in accord with similar observations made in optical reflection studies of KCP (*9*).

To produce samples with a relatively low content of crystal water another part of the original platinum complex was dehydrated in a vacuum at room temperature for several hours until its weight reached a constant value. The loss of water amounted to approximately 10% of the original sample weight corresponding to two water molecules per stacking unit of the platinum chain compound. After dehydration the specimens still had their typical copper sheen but were more brittle than before.

In the following, we refer to the original and the dehydrated samples as to specimens with relatively high and low content of crystal water, respectively. No exact values of *n* can be given in either case.

Results and Discussion

The results of the susceptibility measurements as function of the temperature are shown in Fig. 1. Each curve is the result of at least two independent experiments, the sample weight ranging from 170 to 380 mg. The reproducibility in a single run was better than 1% (for different samples 5%). No field dependence could be detected, neither at room temperature nor at 77 and 4.2°K.

Both the polycrystalline partially oxidized acid, $(H_3O)_{1.6}[Pt(C_2O_4)_2]nH_2O$ with two different values of *n* and the unoxidized potassium salt $K_2[Pt(C_2O_4)_2]nH_2O$ have been measured. The mixed valency compounds are seen to have a diamagnetic and a paramagnetic contribution to their susceptibilities. Except for the lowest temperatures, where a small paramagnetic influence is observed which is most likely due to impurities the unoxidized compound is essentially diamagnetic. This diamagnetism can be well interpreted as the sum of the diamagnetic contributions of the platinum and all ligands estimated on the basis of Pascal's constants. This is also true for the oxidized compounds

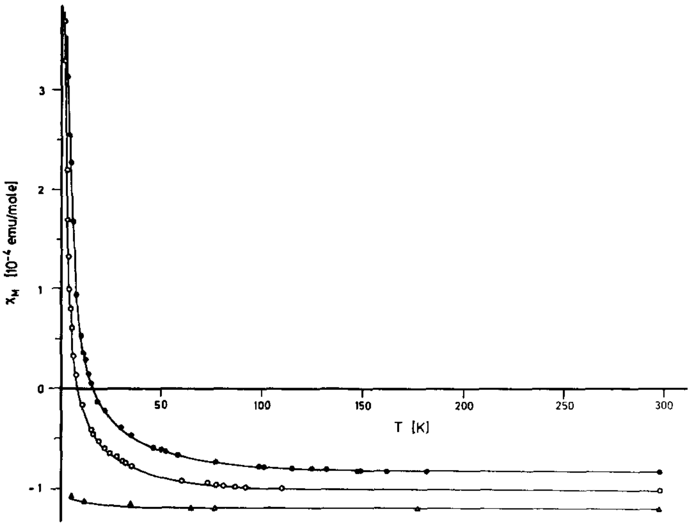

FIG. 1. The molar magnetic susceptibilities, χ_M, of polycrystalline partially oxidized and unoxidized dioxalato platinate complexes as functions of the temperature: ● $(H_3O)_{1.6}[Pt(C_2O_4)_2]mH_2O$ (m is relatively small); ○ $(H_3O)_{1.6}[Pt(C_2O_4)_2]nH_2O$ (n is relatively large); △ $K_2Pt(C_2O_4)_2nH_2O$. In the χ_M-plots n was taken to be w o (*8*) and $m = n - 2 = 0$.

at high temperatures where the paramagnetic contribution is comparably small. In this region, the observed difference of the susceptibilities for compounds with different values of n is essentially due to Pascal's diamagnetic contribution of the crystal water.

As seen from Fig. 2, the paramagnetism of the partially oxidized compounds may be described by two straight lines in the $1/T$ diagram, which have different slopes. From the slopes, we find the effective magnetic moments of the complex with a relatively

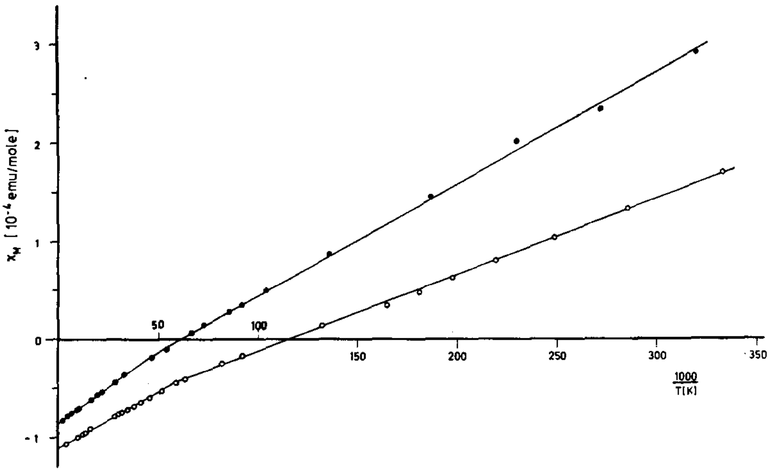

FIG. 2. The molar magnetic susceptibilities, χ_M, of polycrystalline partially oxidized dioxalatoplatinate acids as functions of the reciprocal temperature: ● $(H_3O)_{1.6}[Pt(C_2O_4)_2]mH_2O$ (m is relatively small); ○ $(H_3O)_{1.6}[Pt(C_2O_4)_2]nH_2O$ (n is relatively large). In the $\chi_M(1/T)$-plots n was taken to be two (*8*) and $m = n - 2 = 0$.

large content of crystal water to be 0.097 Bohrs magnetons (BM) above 17°K and 0.079 BM below 17°K. The corresponding values for the complex with a relatively low content of crystal water are 0.11 BM above 22°K and 0.097 BM below 22°K.

We notice a strong effect of the crystal water on the slopes and a small but detectable influence on the temperature where the discontinuity occurs. The weight reduction associated with the loss of crystal water is by far not large enough to account for the observed increase of the paramagnetic susceptibilities per gram of the dehydrated samples in the low-temperature region. Clearly, these findings exclude paramagnetic impurities as possible causes for the observed paramagnetism in the partially oxidized complexes.

The striking similarity between the observed magnetic behavior of $(H_3O)_{1.6}[Pt(C_2O_4)_2]\cdot nH_2O$ and that of KCP (*4*), to which we referred initially, is remarkable. It appears to favor the conclusion that the unusual paramagnetism is a common property of the MVP compounds and possibly associated with the specific electronic structure of the partially oxidized complexes. In fact, no such paramagnetism occurs in the unoxidized analogon.

In principle, metallic properties and Pauli paramagnetism are to be expected after removing a part of the electrons in the top filled d^8 band. Experiments show that except for the Peierls instability the conduction electrons in KCP behave as nearly free electrons in the c direction (*9*).

In terms of the interrupted strand model which treats strand segments bounded by defects as boxes accommodating a one-dimensional electron gas we would expect a Curie type spin paramagnetism of the boxes with an odd number of electrons to dominate at very low temperatures where the spacing of the electron energy levels is much smaller than the thermal energy (*10*) and the Peierls gap is small compared to the level spacing. It must be noted, however, that this concept, for the case of KCP, is difficult to reconcile with the observed anisotropy of the magnetic susceptibility (*4*) and the results of nuclear magnetic resonance experiments in the low-temperature range (*11*, *12*) indicating that the susceptibility observed by Menth and Rice (*4*) is not a property of the conduction electrons of an average Pt strand.

Instead, it has been proposed to assign this susceptibility to localized bonds of structural defects (*1*). In favor of this interpretation one may argue that the observed increase of the susceptibility of $(H_3O)_{1.6}[Pt(C_2O_4)_2]nH_2O$ with decreasing n is an indication that lattice distortions generated by a water deficiency play a role. On the other hand, this assignment is not sufficient to explain the break of the slope in the $1/T$ diagram.

If the Peierls instability prevails at low temperatures, spin paramagnetism may arise from singly occupied states of localized electrons in the Pt-chain. According to Mott (*13*) such states may exist because of the Coulomb repulsion between electrons of different spin in the same localized state. Qualitatively, a localization process of the conduction electrons as a result of a Peierls transition may be considered, therefore, a possible explanation of the change in the slope of the Curie law. However, in view of the above-mentioned NMR results for KCP such an interpretation is also questionable for the dioxalatoplatinate acid.

Another possibility of explaining the observed magnetic discontinuity may be a low-temperature transformation which has been recently suggested to occur in KCP near 35°K by Barmatz et al. (*14*) from the study of elastic properties. Unfortunately, such investigations are not known for the dioxalatoplatinate acid.

It is evident that, at the present state of investigations, no definite conclusion as to the origin of the paramagnetic susceptibility and, in particular, of the observed discontinuity can be drawn. From the present investigation, it is clear that paramagnetic impurities cannot be made responsible for these effects.

References

1. H. R. Zeller, *Festkörperprobleme* **13**, 31 (1973).
2. I. F. Shchegolev, *Phys. Status Solidi* **12a**, 9 (1972).
3. K. Krogmann, *Angew. Chem.* **81**, 10 (1969).
4. A. Menth and M. J. Rice, *Solid State Commun.* **11**, 1025 (1972).

5. A. P. Ginsberg, R. L. Cohen, F. J. DiSalvo, and K. W. West, *J. Chem. Phys.* **60**, 2657 (1974).
6. H. J. Keller (Ed.), "Low-dimensional Cooperative Phenomena and the Possibility of High Temperature Superconductivity," NATO-ASI-Series, Plenum, New York (1975).
7. H. S. Räde, *J. Chem. Phys.* **77**, 424 (1973).
8. H. Wahl, *Chem. News* **62**, 35 (1895); *see also* K. Krogmann and P. Dodel, *Chem. Ber.* **99**, 3416 (1966).
9. H. R. Zeller and P. Brüesch, *Phys. Status Solidi* **65b**, 537 (1974).
10. R. Denton and B. Mühlschlegel, *Solid State Commun.* **11**, 1637 (1972).
11. H. Niedoba, H. Launois, D. Brinkmann, R. Brugger, and H. R. Zeller, *Phys. Status Solidi* **58b**, 309 (1973).
12. H. Niedoba, H. Launois, D. Brinkmann, and H. U. Keller, *J. Phys.* (*Lettres*) **35**, L 251 (1974).
13. N. F. Mott, *Phil. Mag.* **24**, 935 (1971).
14. M. Barmatz, L. R. Testardi, A. F. Garito, and A. J. Heeger, *Solid State Commun.* **15**, 1299 (1974).