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MAGNETOCHEMISTRY: A RESEARCH PROPOSAL

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A. INTRODUCTION

"Magnetochemistry began with Michael Faraday more than one hundred years ago. It enjoyed a vigorous growth at the hands of Langevin, Curie, Weiss, and Pascal; but it did not come of age, so to speak, until Gilbert N. Lewis pointed out, in the early 1920's, the fruitful relationship between magnetic moment and chemical valence." So begins the Preface of the second edition of Selwood's book [1] entitled, Magnetochemistry.

The term "magnetochemistry" first appears in Chemical Abstracts in the year 1912 [2]. The paper in question, apparently a thesis, reported on the "Magnetochemie Beziehungen zwischen magnetischen Eigenschaften u. chemischer Natur." Chemists have been looking for magneto–structural correlations [3] for a long time! The first books entitled Magnetochemistry appeared in the thirties [4–6], and there have been a number of other books and reviews with "magnetochemistry" in their titles since then: some of them are listed in refs. 7–12. Examination of these texts and comparison with my recent text of the same name [13] shows at least two trends that are emerging with the passage of time: first, a continual decrease in working temperature, such that measurements at liquid helium temperatures are now commonplace, and second, as theory and experiment have progressed, the subject of paramagnetism has been essentially worked out, and study of the interactions between metal ions has come to dominate the field. One significant feature, which has suffered a decrease in interest among chemists

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with time, concerns the study of metals and alloys. This is unfortunate, for the field is a rich one. Nevertheless, this paper will be concerned with what the physicist calls insulators, and the chemist, coordination compounds. Magnetic ordering and the chemical and structural features which control it are now the dominating topics of interest in this field.

I have recently reviewed at length the current status of magnetochemistry [13]. Several, more specialized articles have also appeared, on the magnetochemistry of the $^4A_2$ state [14], on the $A_2[FeX_5(H_2O)]$ series of antiferromagnets [15], and on the structural and magnetic properties of the pyridine *N*-oxide complexes of the transition metals [16]. This article will be concerned with my opinions about several areas where further progress could be made, and the kind of work I hope to be doing during the next few years. Additional details and references to the literature may be found elsewhere [13].

B. BIMETALLIC COMPOUNDS

We have recently become interested in what we call bimetallic compounds, that is, materials in which two different metal ions occur in some ordered arrangement. An artificial magnetic structure may thus be constructed; these are well-defined chemical compounds, rather than either mixtures or solid solutions. A serendipitous example is provided by $CoCl_2 \cdot 3C_5H_5NO$, which is actually $[Co(C_5H_5NO)_6](CoCl_4)$, and in which both the cation and anion are coordination compounds. The ligand C_5H_5NO is pyridine *N*-oxide [17,18]. Other, synthetic examples are provided by $[Cr(H_2O)(NH_3)_5][Cr(CN)_6]$ and $[Cr(NH_3)_6][Cr(CN)_6]$ [19–21]. Either metal ion may be diamagnetic as well, as exemplified by $[Co(C_5H_5NO)_6](ZnCl_4)$ and $[Co(NH_3)_6][Cr(CN)_6]$.

TABLE 1

Crystal structure analyses of some bimetallic compounds

Compound	Space group	Ref.
$[Cr(H_2O)(NH_3)_5][Cr(CN)_6]$	$R\bar{3}$	22
$[Co(C_5H_5NO)_6](CoCl_4)$	Cc	18
$[Cr(en)_3][Co(CN)_6] \cdot 6H_2O$	$I2/a$	23
$[Cr(NH_3)_6][CuCl_5]$	$Fd3c$	24
$[Co(NH_3)_6][CuCl_5]$	$Fd3c$	25
$[Co(NH_3)_6][FeCl_6]$	$R\bar{3}c$	26
$[Fe(bpy)_2Cl_2][FeCl_4]$	$P2_12_12_1$	27
trans-$[Cr(en)_2(H_2O)_2]$–*trans*-$[Cr(en)_2(OH)F]_2(ClO_4)_5 \cdot 2H_2O$	$C2/c$	28

Preparations are usually carried out using simple metathetical reactions such as

$$[Cr(NH_3)_6]Cl_3 + K_3[Cr(CN)_6] \rightarrow [Cr(NH_3)_6][Cr(CN)_6]$$

The combination of large cation with large anion however, causes many of these materials to be sparingly soluble, which in turn renders single-crystal growth difficult. Crystal structure analyses of a variety of bimetallic compounds, some of which are listed in Table 1, have shown that the compounds are indeed as described above.

One of the original goals of our studies on these samples was to determine if the increased concentration of magnetic ions in bimetallic compounds when compared to such compounds as $[Cr(NH_3)_6]Cl_3$ would enhance the exchange interaction and thus increase the ordering temperature. Ordering has not yet been reported in hexamminechromium(III) chloride, and T_c is expected to be below 1 K; we have recently found that $[Cr(en)_3]Br_3 \cdot 4H_2O$ orders (antiferromagnetically) at only 110 mK. It was found that the exchange is indeed stronger in both $[Cr(H_2O)(NH_3)_5][Cr(CN)_6]$ and $[Cr(NH_3)_6][Cr(CN)_6]$ with respect to the analogous compounds in which one of the chromium atoms is replaced isomorphously by diamagnetic cobalt(III), as in $[Co(NH_3)_6][Cr(CN)_6]$, for example. Nevertheless, the ordering temperatures in these particular compounds are still quite low. Some bimetallic compounds which undergo long-range ordering are listed in Table 2. What turns out to be more interesting is that both of the Cr/Cr compounds listed above appear to order as ferromagnets, rather than as the anticipated antiferromagnets: some of the data are illustrated in Fig. 1. Furthermore, the previously mentioned $[Co(C_5H_5NO)_6](CoCl_4)$ orders as a canted antiferromagnet, although the analogous bromide salt does not

TABLE 2

Some bimetallic magnets

Compound	T_c(K)	Ref.
$[Cr(urea)_6][Cr(CN)_6] \cdot 3H_2O$	0.300	19
$[Cr(H_2O)(NH_3)_5][Cr(CN)_6]$	0.380	21
$[Cr(NH_3)_6][Cr(CN)_6]$	0.60	21
$[Co(C_5H_5NO)_6](CoCl_4)$	0.95	18
$[Co(C_5H_5NO)_6](ZnCl_4)$	0.95	18
$[Co(C_5H_5NO)_6](CoBr_4)$	0.65	18
$[Co(C_5H_5NO)_6](ZnBr_4)$	0.65	18
$[Co(NH_3)_6][FeCl_6]$	~ 0.9	30
$[Cr(NH_3)_6][FeCl_6]$	2.85	29
$[Cr(H_2O)(NH_3)_5](CuCl_5)$	0.298	20

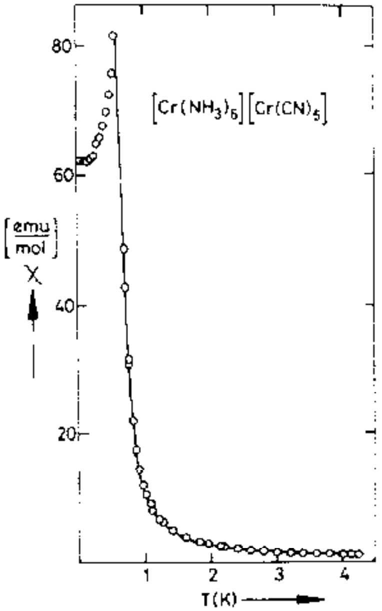

Fig. 1. Experimental zero-field magnetic susceptibility of powdered $[\mathrm{Cr(NH_3)_6}][\mathrm{Cr(CN)_6}]$. The curve has been calculated for Heisenberg ferromagnetic exchange, $S = 3/2$, in a body-center-cubic lattice with $J/k_B = 0.042$ K, and correcting for demagnetization effects. From ref. 21.

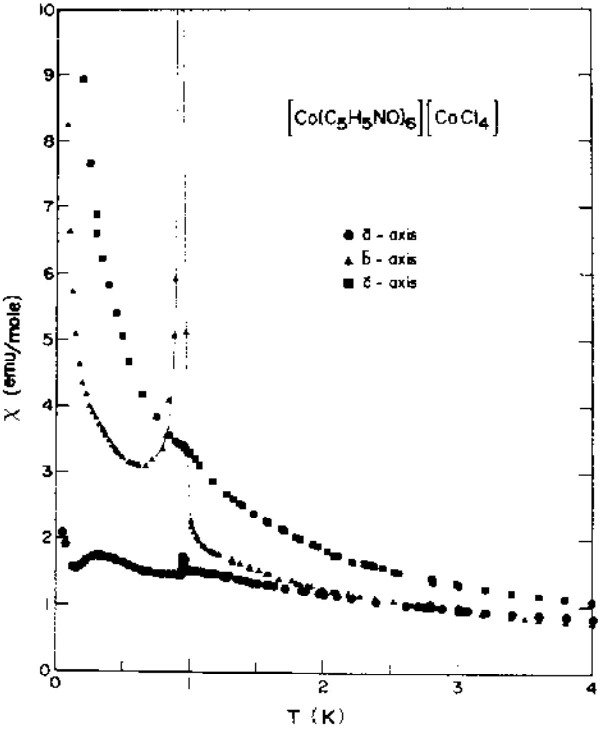

Fig. 2. Susceptibility data parallel to the three crystallographic axes of $[\mathrm{Co(C_5H_5NO)_6}](\mathrm{CoCl_4})$. The maximum value of χ as measured in the b-direction at $T = T_c$ equals ~100 emu/mol. From ref. 18.

TABLE 3

Some insulating ferromagnets

Compound	T_c(K)
$K_2CuCl_4 \cdot 2H_2O$	0.88
$Rb_2CuCl_4 \cdot 2H_2O$	1.02
$Rb_2CuBr_4 \cdot 2H_2O$	1.87
$FeCl[S_2CN(C_2H_5)_2]$	2.46
$NiSiF_6 \cdot 6H_2O$	0.135
$NiTiF_6 \cdot 6H_2O$	0.14
$CrCl_3$	16.8
$CrBr_3$	32.7
CrI_3	68
$GdCl_3$	2.20
$ErCl_3$	0.307
$DyCl_3 \cdot 6H_2O$	0.289
$ErCl_3 \cdot 6H_2O$	0.356
EuO	69

exhibit canting. The octahedral and tetrahedral sublattices in these Co/Co materials are independent and do not interact magnetically. The susceptibilities of $[Co(C_5H_5NO)_6](CoCl_4)$ are illustrated in Fig. 2. Why any of these materials order in the way that they do is not clear at this time.

Thus, it is my opinion that one of the major questions remaining in magnetochemistry research is to discover the ground rules for constructing new ferromagnets. The majority of magnetically ordered coordination compounds are antiferromagnets, but more and more ferromagnets have been found as time progresses. One advantage of studying ferromagnetic insulators is that one can carry out experiments over the entire range of the electromagnetic spectrum, without interference from eddy currents. Several examples are listed in Table 3. An orthogonal exchange path is often cited as the source of a ferromagnetic interaction but, except for dimers, one is rarely as yet in a position to control the exchange path. A number of bimetallic coordination compounds do exhibit ferromagnetism, and I believe it will be profitable to explore this phenomenon further by the study of more bimetallic compounds.

Bimetallic compounds also provide, at least potentially, a way to find new ferrimagnets, of which there are otherwise relatively few. Ferrimagnets are generally defined as antiferromagnets in which one magnetic sublattice does not compensate the other. A variety of spin arrangements are possible in ferrimagnets, depending on the number and kind of sublattices and their relative orientations. This can be found when the ions on the two sublattices differ in their coordination environment, their chemical nature or their spin.

One expects substances such as $[Cr(NH_3)_6][FeC]_6]$ and $[Cr(NH_3)_6][CuCl_5]$ [25,29,31], which contain magnetic ions of differing spin, to order as ferrimagnets and the former compound indeed seems to do so [29]. The ordering temperature of $[Cr(NH_3)_6][FeCl_6]$ is not as low as might have been anticipated. We have reported some measurements on $[Cr(H_2O)(NH_3)_5][CuCl_5]$ [20]. The type of compounds described here offer several potential advantages over the classical ferrimagnets such as the spinels and garnets. Chemical composition and metal valence can be controlled more precisely and the lower ordering temperatures will allow experiments such as specific heat measurements to be carried out more profitably in future.

The two groups of materials, ferromagnets and ferrimagnets, may be considered together. The planned synthesis (or so-called "molecular engineering") of the appropriate ordered materials is still more an art than a science. The unifying theme here is the existence of a permanent moment in the ordered state.

Bimetallic compounds are of more general interest. It is intriguing that the salt $[Co(pn)_3][FeCl_6]$, where pn is 1,2-propanediamine, appears to order (antiferromagnetically!) at a higher temperature (about 9 K) than the less-sterically hindered $[Co(NH_3)_6][FeCl_6]$ [30,32]. It would be interesting then to compare $[Cr(NH_3)_6][FeCl_6]$ with $[Cr(pn)_3][FeCl_6]$ in order to see if the trend persists; the latter compound should order at a relatively high temperature. One would also want to examine $[Cr(en)_3][FeCl_6]$ (en is ethylenediamine) as well, and we are currently doing that. We are by no means limited to chromium complexes, though there are so many of these that the restriction does not appear to be severe. We are limited only by the synthesis of suitable materials, preferably in single crystal form. Other materials worthy of examination would include substances such as $[Cr(NH_3)_5Cl][Cr(NH_3)Cl_5]$, for example; the purpose of all the chloride ligands is to enhance the exchange interaction and thus increase T_c. One can imagine other substances such as $[Mn(C_5H_5NO)_6](MnCl_4)$ (both ions have $S = 5/2$) in order to examine the effect of a change in the spin, as well as, say, $[Cr(H_2O)_5Cl][Fe(H_2O)Cl_5]$.

Others have been studying bimetallic chain complexes such as $Ni_2(EDTA) \cdot 6H_2O$ [33–37], $NiCo(EDTA) \cdot 6H_2O$ [35,38], $Co_2(EDTA) \cdot 6H_2O$ [39] and $CuMn(S_2C_2O_2)_2 \cdot 7.5H_2O$ [40,41]. As might be expected, the Ni/Co salt, in which ions of differing spin alternate in the chain, is a one-dimensional ferrimagnet [38]. The Ni/Ni salt is also a ferrimagnet by virtue of the fact that the nickel ions are coordinated differently; it has also been shown [36] that nickel ions with different *g*-values at the different (alternating) sites will be ferrimagnets.

Dimers present the simplest examples for the study of exchange interactions. Recent work on binuclear complexes has been reviewed [42]; several bimetallic materials have been studied. The range of possibilities offered by inorganic chemistry is emphasized by the recent [43,44] studies on several bimetallic compounds of another kind, which contain the trinuclear Cu–Gd–Cu moiety in the cation. The synthesis of such materials is straightforward, and the interesting point for our purposes was the demonstration of the fact that the Gd–Cu exchange interaction, which varies from compound to compound, is about 1–7 cm^{-1} ($J/k \sim 2$–10 K) in strength and ferromagnetic in sign. It would be exciting to be able to study compounds such as these with the interactions extended throughout the lattice.

Incidentally, we emphasize transition temperatures here for characterizing a system rather than exchange constants for two reasons. The transition temperature T_c is in fact related to the exchange constant J/k by, say, the molecular field relationship

$$T_c = 2S(S+1)zJ/3k$$

where z is the (generally unknown) magnetic coordination number for a given system. More importantly, T_c is a directly measured empirical quantity, while some kind of model must always be invoked in order to determine the exchange constant.

C. 4*d* AND 5*d* METALS

Let us turn now to another topic, a general discussion of the chemistry and physics of the heavier metals. There are several well-known features of these metals which I mention here for the sake of completeness. The size of the 4*d* and 5*d* ions, when in the same column, is about the same. In striking contrast with the iron series of ions, the aquo ions of the divalent and trivalent metal ions are rare. Spin–orbit coupling and strong crystalline fields cause all the paramagnetic compounds to be low-spin, and most of these have spin $S = 1/2$. Nickel forms many paramagnetic octahedral complexes, taken as a typical example, but neither of its congeners, palladium and platinum, does.

Also fewer oxidation states are available; for example, cobalt(II) is exceedingly important in magnetism, while only a few rhodium(II) compounds are known. The heaviest member of the family, iridium(II), is unknown. Similar behavior is observed with the copper–silver–gold triad.

Iridium(IV) has been extensively studied, especially as $(NH_4)_2[IrCl_6]$ and $K_2[IrCl_6]$, which are well-known antiferromagnets. These salts are cubic, however, and there have therefore been no measurements of single-crystal susceptibilities. Iridium(IV) is expected to be anisotropic, and so we have been searching for iridium salts with a lower crystal lattice symmetry. There are very few other studies on 4*d* or 5*d* metal complexes [13].

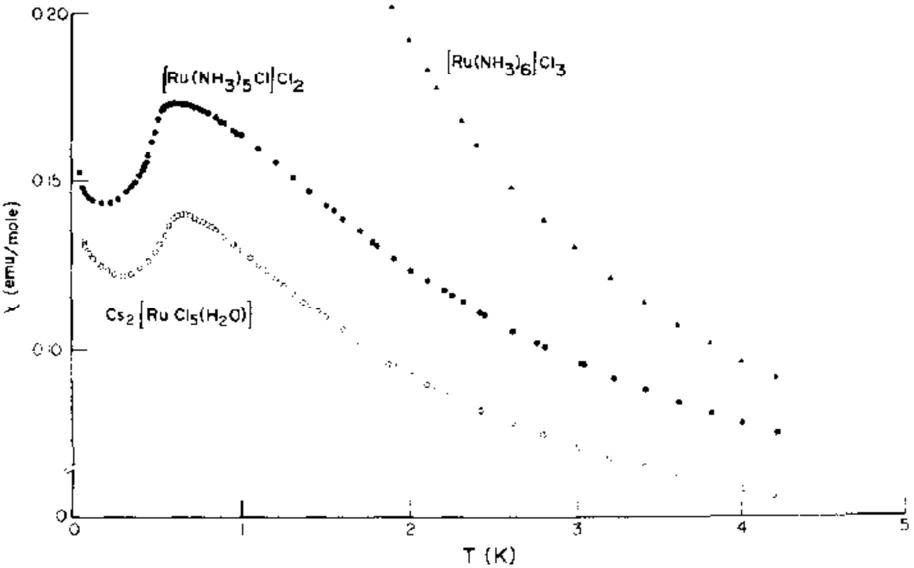

Fig. 3. The magnetic susceptibilities of antiferromagnetic $[Ru(NH_3)_5Cl]Cl_2$ and $Cs_2[RuCl_5(H_2O)]$, compared with that of paramagnetic $[Ru(NH_3)_6]Cl_3$. (The increase in the magnitude of the susceptibility at low temperatures is due to the paramagnetic impurities.) From ref. 45 and 46.

Molybdenum(III) is a well-known species, but there are no well-characterized ordered magnets of this ion as yet. Preliminary studies [45] on the $S = 3/2$ material $(NH_4)_2[MoBr_5(H_2O)]$ yield the relatively high transition temperature of about 12 K. The only thorough magnetic study to date on osmium(III) appears to be an EPR study of a phosphine complex; measurements [45] on $[Os(NH_3)_5Cl]Cl_2$ indicate that T_c is about 1 K.

There are as yet no examples among the 4*d* or 5*d* metals of any linear chain or planar magnets, nor do there seem to be many studies of dimers (à la copper acetate.) The growth of macroscopic single crystals is also difficult.

The susceptibility of several ruthenium salts [45,46] is illustrated in Fig. 3. Our susceptibility measurements on ruthenium(III) salts, which have very anisotropic *g*-values, appear to be the first such single-crystal measurements at low temperatures. The results to date are unusual, for the easy axis susceptibility of $[Ru(NH_3)_5Cl]Cl_2$ is lower in magnitude than the perpendicular susceptibilities; this is unusual behavior and may be evidence for true anisotropic exchange. It is these results that have stimulated our interest in examining the heavier metals more extensively in order to see how general is this result. Specific heat measurements [47] on both $[Ru(NH_3)_5Cl]Cl_2$ ($T_c = 0.525$ K) as well as $Cs_2[RuCl_5(H_2O)]$ ($T_c = 0.58$ K) are as yet incomplete. The latter compound belongs to the $A_2[RuX_5(H_2O)]$ series of antiferromagnets [45], which appear to be isomorphous to the analogous

$A_2[FeX_5(H_2O)]$ series of antiferromagnets [15]. The number of compounds potentially available for study is much smaller than among the iron series ions; the only relevant ions known to date are Mo(III), Ru(III), Re(IV), Os(III) and Ir(IV). Neither silver(II) nor gold(II) form enough magnetically concentrated and well-characterized materials to be of interest at the moment.

It is clear that a major program of synthesis of paramagnetic compounds of the 4*d* and 5*d* metals would be quite profitable. Perhaps the desired compounds have not yet been prepared simply because of the expense the raw materials for a synthetic research program would incur. Unfortunately, we are generally looking for larger sample quantities than are required by the organometallic chemists who have studied these elements so thoroughly.

D. RARE EARTHS

The common oxidation state for these is three, and we do not concern ourselves here with the magnetic superconductors. The hydrated ions are the commonest; oxygen, nitrogen and halide are the favored donor atoms. High coordination numbers are common, with eight-coordination being the commonest. Six-coordination, found so often with the iron-series ions, is rare. The result of the high coordination numbers, in conjunction with the bulk of the typical ligands, as well as the shielding of the 4*f* electrons by the outer shells is to decrease the importance of superexchange paths. Thus dipolar coupling dominates most compounds studied to date, which typically order at well below 1 K.

Spin–orbit coupling dominates the crystal field splittings, and non-Kramers ions are common. Therefore, the ground state can rarely be characterized by a single value of the total quantum number J. The g-values are often quite anisotropic and deviate substantially from 2. EPR can usually be observed only at temperatures of 20 K or below. The non-Kramers ions may have a singlet ground state, and thereby yield neither an EPR spectrum nor magnetic ordering.

As a result of the structural chemistry of the rare earths, there are as yet no low-dimensional magnets, as are found so frequently with the iron-series ions, except a few accidental ones. The problem here is to prepare new compounds with, say, bridging ligands between two or more metal ions so that superexchange interaction can become effective. That this is possible can be illustrated by the ordering temperatures of a number of anhydrous rare earth compounds that are high enough to require the presence of such interactions. The europium chalcogenides order at high temperatures, and the series of compounds R_2ZrS_5 order [48] at 4.5 (Sm), 12.74 (Gd), 9.27 (Tb), 5.24 (Dy) and 2.52 K (Er).

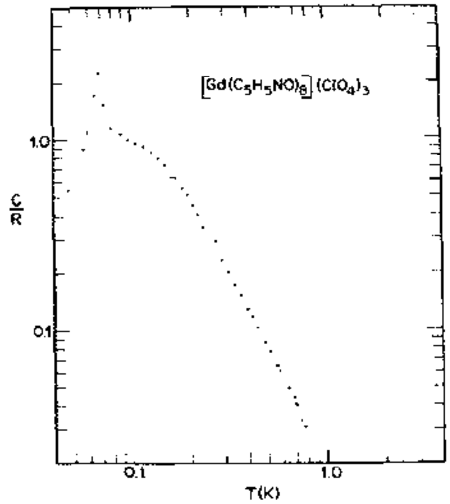

Fig. 4. Specific heat of $[Gd(C_5H_5NO)_8](ClO_4)_3$. From ref. 49.

The specific heat and susceptibility of $[Gd(C_5H_5NO)_8](ClO_4)_3$ have been measured [49] and are illustrated in Figs. 4 and 5. The salt undergoes antiferromagnetic ordering at 70 mK. Attempts to prepare analogous compounds of the other rare earths have been fruitless to date.

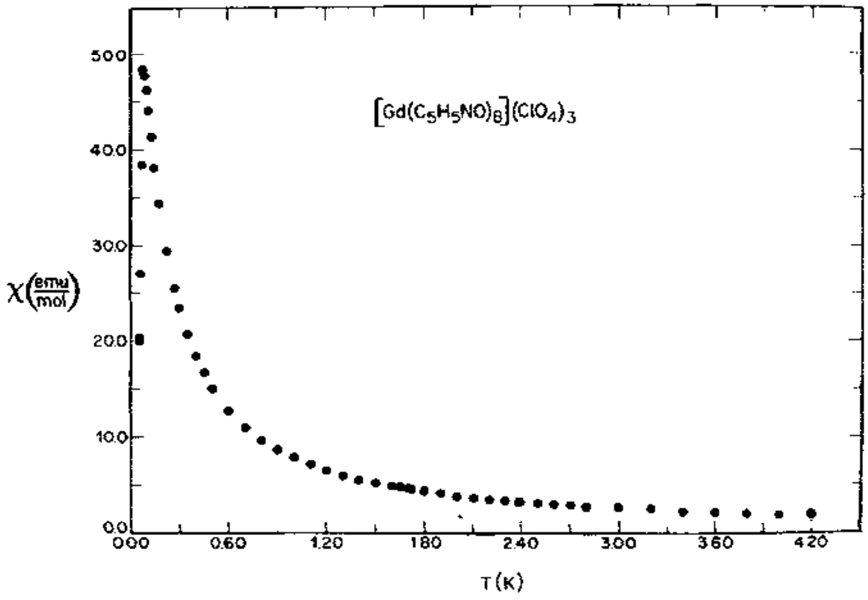

Fig. 5. Magnetic susceptibility of polycrystalline $[Gd(C_5H_5NO)_8](ClO_4)_3$. From ref. 49.

E. CONCLUSIONS

The work described lies on the borderline between inorganic chemistry and solid state physics; indeed, some of the most notable recent advances in magnetochemistry have come about by the collaborative efforts of groups of physicists and chemists. One notices that the physicists generally prefer to examine a problem from first principles ("I need a compound that will exhibit the property − − −"), while a chemist, as is to be expected, tends to be interested in the particular compounds, per se ("I have made a copper compound that has the structure − − −. Do you think it might be interesting?") Chemists tend to reason by analogy, and as illustrated above, use the periodic chart extensively. An article complementary to this one, which considers many problems remaining in the field of binuclear complexes, is that by Kahn [42].

We need more new compounds! There are very few XY antiferromagnets, of any lattice dimensionality, and most of the known XY magnets have ordering temperatures below 1 K. It would be convenient, for the purposes of a variety of studies, to have some such materials with a higher T_c. Few magnetic materials with $S = 3/2$ have been studied, and we could use some $S = 3/2$ linear chains, as well as superexchange-coupled materials in general. There are few, if any, $S = 5/2$ ferromagnetically aligned linear chains. The zero-field splitting (ZFS) in molybdenum(III) is supposed to be an order of magnitude greater than that in its congener chromium(III), yet there are few if any measurements which corroborate this. This is true, even though a ZFS of that size will control the magnetic ordering in molybdenum compounds.

Although it was observed earlier that chemists have not lately been interested in the magnetic properties of metals, this may change in the near future. This is due to the emerging interest in metal particles and large metal clusters [50].

An area of current interest in physics that has not been touched upon here concerns disordered materials [51]. This subject encompasses such subjects as metallic (and nonmetallic) spin glasses, amorphous magnets and random alloys. Another subject not discussed here concerns spin–crossover transitions.

Finally, chemists have now to do more in the way of the determination of microscopic magnetic structures. The determination of spin structures at low temperatures by NMR or neutron scattering are two experiments that come to mind. Physicists who did these experiments have moved on to other problems, so it is now up to chemists to undertake more of this kind of work. We point out, for example, the two closely-spaced λ-peaks which appear at zero field in the specific heat of $Cs_2[FeBr_5(H_2O)]$; these are suggestive of a spin–reorientation transition [15]. Neither susceptibility nor specific heat measurements alone are capable of discerning the source of the two peaks, but other, more sophisticated techniques must be used. This will require more expensive experiments, as well as more people who are closer to today's physics.

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