Metamagnetism in tetrachlorobis(*N*-phenylacetamidine)rhenium(IV) †

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Single-crystal magnetisation and polarised neutron diffraction (PND) measurements have been made for the complex *cis*-$[ReCl_4(NH{=}CMeNHPh)_2]$. At higher temperatures the magnetic behaviour is typical of such a rhenium-(IV) complex, with three unpaired spins ($\mu = 3.6\ \mu_B$), an almost isotropic *g*-tensor of 1.86(1) and a large zero-field splitting, $2D$, of $-20(2)\ cm^{-1}$. At very low temperatures the magnetisation behaviour as a function of temperature and field strength and direction indicates two magnetically ordered structural phases when $H \| b$, but only one for *a* and *c*, with $T_N = 9.7(1)$ K. A tricritical point at $T = 5.8(2)$ K and $H = 4.40(5)$ *T* was established on the transition line in *H vs. T* space between the two phases when $H \| b$. This behaviour is metamagnetic. The two-dimensional form of the stronger magnetic exchange implied, with weaker interlayer interaction, can be correlated with the observed structural feature of *ab* planes of $ReCl_4$ units separated by layers of phenyl rings. The PND experiment showed that about half of the spin of the system is delocalised away from the Re by covalent bonding to the Cl atoms and the amidine ligand, accompanied by considerable effects resembling spin polarisation. The magnetic space groups are $P2_1/c$ at low magnetic fields and $Pc2_1n$ at high fields along *b*, compared with the nuclear structural space group of *Pccn*.

Metamagnets are systems in which competing magnetic interactions are such that, at any temperature below the Neel point, the application of a modest magnetic field causes a sudden transition from an antiferromagnetic phase to one with a ferromagnetic component, often an aligned paramagnet.[1] Spin-flop materials are related in type, but are distinguished by the presence of the spin-flop phase, which results in two characteristic and different magnetisation behaviours.[2] Previous examples of metamagnets have generally been simpler materials, *e.g.* $[NMe_3H][CoCl_3]{\cdot}2H_2O$[3] and $CsCoCl_3{\cdot}2D_2O$,[4] although $[Fe(C_5Me_5)_2][tcnq]$[5] (tcnq = tetracyanoquinodimethane) and a manganese Schiff base–ferricyanide complex[6] are notable exceptions. We have prepared and examined a new system. It is of interest since there appears to be a possibility of tuning the metamagnetic behaviour in desirable ways by substitution of its amidine ligand. Indeed the initial preparations of Rouschias and Wilkinson[7] involved various substituted related ligands, but neither their magnetic behaviour nor their crystal structure is known.

Our investigation of covalent bonding in heavy transition-metal complexes by polarised neutron diffraction (PND) to measure the magnetisation density in crystals in an applied magnetic field began with the study of a caesium molybdenum(III) alum,[8] and has continued with $[AsPh_4][TcNCl_4]$[9] and tris(acetylacetonato)ruthenium(III).[10] The studies require large single crystals of the relatively simple molecules, and are mostly difficult to obtain. Compounds of formula $[ReCl_4L_2]$ (L = ligand)[11] show promise of availability in the form of large single crystals, and are often of the high-spin category, which is unusual for heavy-metal compounds. The high-spin feature is a strong advantage for accuracy in the PND experiment.

We therefore prepared, amongst other compounds, crystals of $[ReCl_4(NH{=}CMeNHPh)_2]$, which can be grown to large sizes.[7,12] It proved to be unsuitable for our primary aim of PND studies, the examination of covalence, due to its unusual magnetic behaviour. However this behaviour established it as a metamagnet. Since such systems are uncommon, particularly in heavy-metal compounds, we proceeded with extensive magnetisation and PND measurements.

Experimental

Preparation

The compound $[ReCl_4(NH{=}CMeNHPh)_2]$ was prepared by reaction of $[ReCl_4(NCMe)_2]$[7] with aniline in acetone solution, with a yield of 70% of good uniform crystalline material [Found (Calc.): Cl, 23.7 (23.8); Re, 32.8 (31.2%)]. Single crystals of this stable complex were grown by evaporation of a solution of it in acetone. Relatively isometric crystals up to 50 mg in weight were obtained, with, surprisingly, (413) the major faces and (100), (001) and (110) the minor faces.

Bulk magnetic measurements

The magnetisations of single crystals with weights from 4.8 to 6.1 mg mounted along *a*, *b* and *c* were measured between 2.0 and 300 K at applied magnetic fields up to 5 T using a SQUID magnetometer (Quantum Design, San Diego, CA). The crystals were aligned gluing them in niches in 3 mm diameter Perspex rods to an accuracy of better than 2°, as estimated by optical goniometry. Initially, a general survey of the *H*–*T* plane (*H*, magnetic field; *T*, temperature) was made for each crystal orientation. Interesting regions were subsequently filled in with a closer mesh of observations. In particular, a search was made to locate the tricritical point by successively finer scans in both *T* and *H*. In addition, scans in both *H* and *T* close to the phase boundary were made to eliminate the possibility of other phase boundaries. The data were corrected for the diamagnetism of the glue, the niche in the rod, and for the molecular diamagnetism ($-269 \times 10^{-12}\ m^3\ mol^{-1}$) to give the paramagnetic components of the molar magnetisation. The data were converted into magnetic moment and magnetisation data, expressed in Bohr magnetons. Fig. 1 shows the principal magnetic susceptibilities, Fig. 2 the magnetic field dependence of the induced moment at various temperatures and Fig. 3 scans close to the tricritical point.

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† *Non-SI unit employed:* $\mu_B \approx 9.27 \times 10^{-24}\ J\ T^{-1}$.

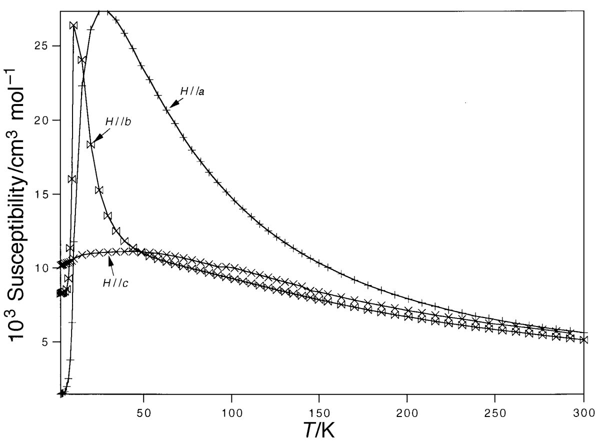

Fig. 1 Principal magnetic susceptibilities *versus* temperature using a magnetic field of 1.0 T

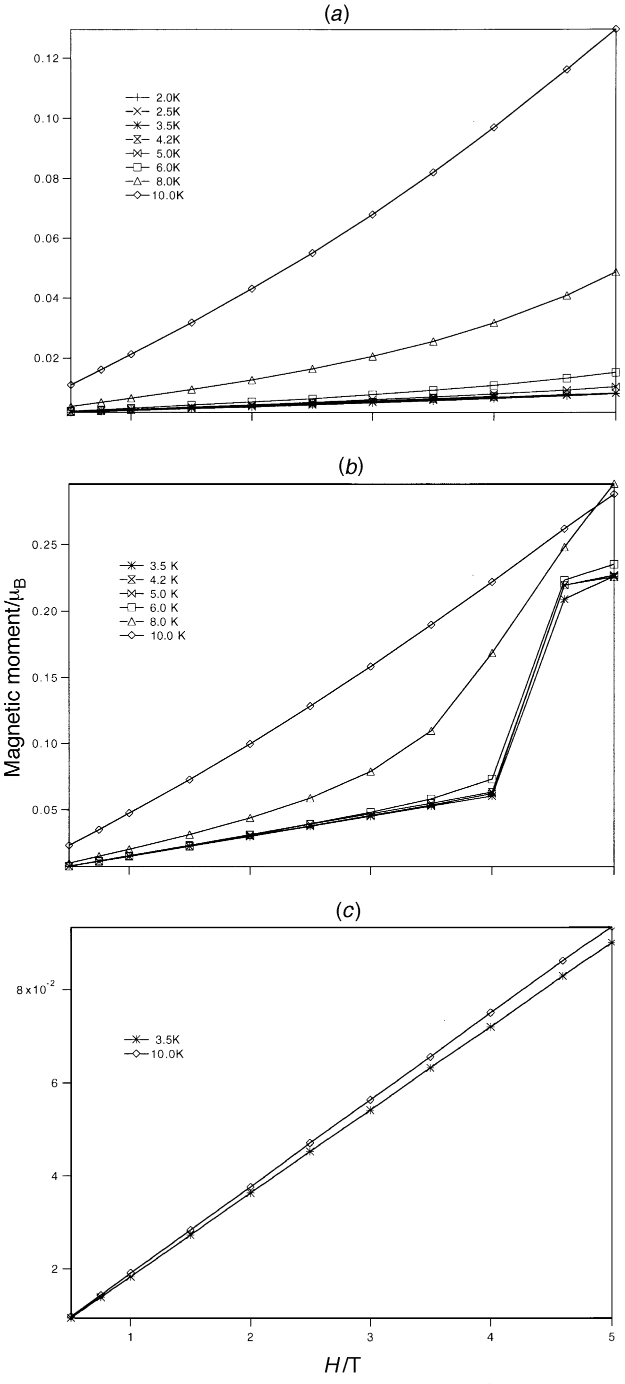

Fig. 2 Magnetisations (per rhenium) *versus* magnetic field at various temperatures along *a* (*a*), *b* (*b*) and *c* (*c*)

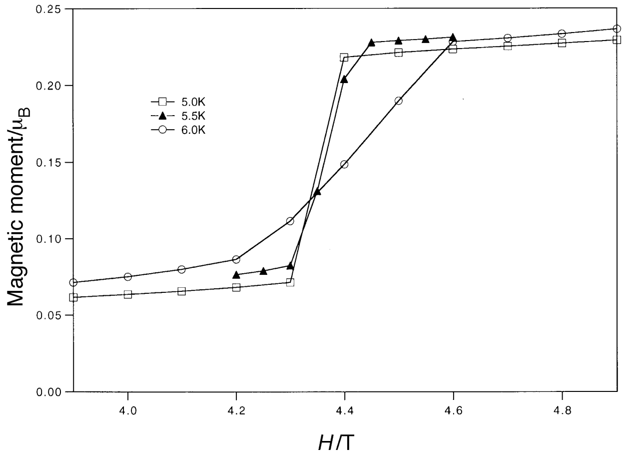

Fig. 3 Detail of the magnetisation behaviour near the tricritical point, magnetic field along *b*

Neutron diffraction

The PND experiment was performed at the HFIR reactor of the Oak Ridge National Laboratory, on spectrometer HB1, with a wavelength of 1.068(1) Å. Neutron polarisation was achieved by use of an iron–silicon monochromator which gave a polarisation efficiency of 0.91(1). A 41 mg crystal was used, mounted with *b* parallel to the vertical applied magnetic field. All reflections were centred manually before counting intensities for the determination of flipping ratios. The flipping ratio is the ratio of observed diffracted Bragg intensities with neutron spin, respectively, parallel and antiparallel to the applied magnetic field. From these data we obtained two cell constants at 4.18 K, $a = 21.5(1)$ and $c = 12.48(3)$ Å, which are consistent with the X-ray values at 92 K.[12] Flipping ratios were obtained from 28 ($h0l$) intense reflections, which after averaging symmetry equivalents gave the 21 unique flipping ratios. If the nuclear structure factors are known, in this centrosymmetric structure, then we can calculate values for the *z* component of the magnetic structure factor for the reflections which are all in the basal plane of the diffractometer. The nuclear structure factors were estimated by extrapolation from the 92 K X-ray-determined structure, decreasing thermal parameters and adjusting coordinates for unit-cell changes. The C—H bond lengths were increased to 1.05 Å to correct for the well known apparent shortening observed by X-ray diffraction. The error introduced by this procedure, compared to the more usual use of experimental unpolarised neutron data, is consistently less than the errors introduced from the flipping-ratio data. The *z* components of the magnetic structure factors are listed in Table 1. The errors include the uncertainty in the nuclear structure factor.

We have also performed two subsidiary sets of unpolarised intensity measurements. Eight reflection intensities forbidden in the *Pccn* space group were measured at 4.2 K and at magnetic fields along *b* of both 3.5 and 5 T. We also measured the intensities of 10 allowed reflections at 14 K, then at 4.2 K with no magnetic field. Significant magnetic intensities were not observed in either case.

Results and Discussion

Structure

The present compound, with L = NH=CMeNHPh, at 92 K has space group *Pccn* with $a = 21.677(4)$, $b = 7.235(1)$, $c = 12.470(2)$ Å, $Z = 4$. The structure is discussed in more detail elsewhere;[12] here we present only a summary of relevant details. The Re atom is *cis*-octahedrally co-ordinated by 4 Cl and 2 N atoms. The Re—N and mean Re—Cl bond lengths are 2.077(2) and 2.361 Å respectively. The amidine–rhenium–amidine

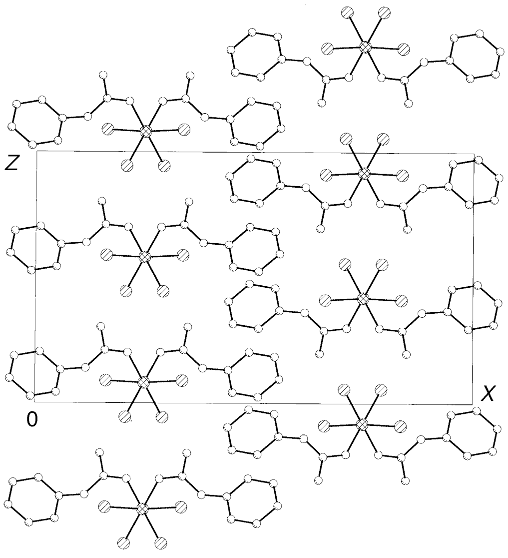

Fig. 4 The *ac* projection of the unit cell showing the [ReCl$_4$(NH=C-MeNHPh)$_2$] molecular dispositions

Table 1 The *z* components of the magnetic structure factors, observed and calculated ($\mu_B \times 10^3$)

h*	l	F_{obs}	F_{calc}
0	0	904(10)	902
1	2	−404(17)	−416
4	0	339(26)	348
3	2	487(39)	481
4	2	103(19)	113
6	0	−207(28)	−235
5	2	−348(30)	−286
0	4	−181(97)	−150
1	4	−484(65)	−257
2	4	120(46)	245
3	4	203(23)	223
7	2	111(23)	146
4	4	−56(45)	−39
8	0	241(25)	177
6	4	80(32)	5
10	0	0(38)	−111
2	6	181(39)	216
9	4	−139(30)	−50
12	0	146(27)	97
10	4	−27(40)	35
11	4	−148(30)	−148
0	8	220(110)	35

* $k = 0$ throughout.

fragment has an extended conformation which facilitates separation of the hydrophobic amidine and hydrophilic ReCl$_4$ in the structure. It can be described as sheets of ReCl$_4$ units in the *bc* plane separated by layers of phenyl rings which are themselves twisted at approximately right angles to the Re−N−C−N plane. The Re···Re separations are 7.25 and 6.25 Å along *b* and *c* respectively, but much longer along *a*. The [ReCl$_4$(NH=C-MeNHPh)$_2$] molecular packing in the unit cell is illustrated in Fig. 4.

Bulk magnetism

Single-ion properties. The Re^{IV} is *cis* co-ordinated by two amidine ligands, with the other octahedral positions occupied by chlorine atoms. Although a little encountered ligand, *N*-phenylacetamidine is typical of many N-ligating ligands with no particularly unusual properties. Given the substantially higher position of amine than chloride in the spectrochemical series, and their differing π-donor nature, we may expect a substantial tetragonal crystal-field component with its unique axis along the Re−Cl(1) bond direction. We note the substantial spin–orbit coupling constant which, after allowing for reduction by covalence, is about 1600 cm^{-1} in magnitude. It can then be predicted that the degeneracy of the $^4A_{2g}$ ground state is removed by a substantial amount of zero-field splitting. Use of the program BFDN,[13] with 5d energy splittings estimated from standard spectrochemical tabulations[14] ($10Dq = 30\,000$, t_{2g} splitting 3600 cm^{-1}) gives a zero-field energy splitting, $2D$, of about -10 cm^{-1}, which leads to a $J = \frac{3}{2}$ ground state.

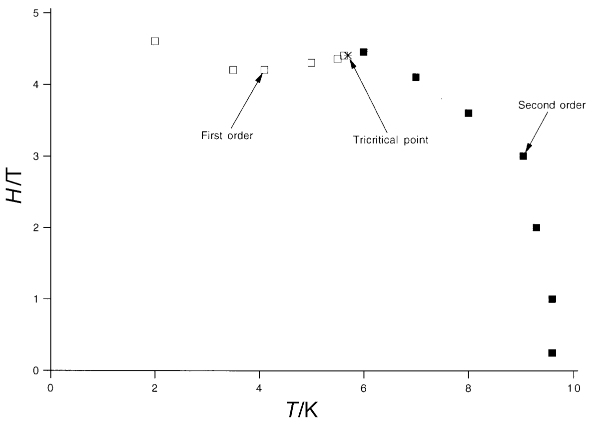

Fig. 5 Magnetic phase diagram in the magnetic field–temperature plane, above 2 K with the magnetic field along *b*. The open squares show points measured as a first-order metamagnetic transition, the closed are second-order points, while the asterisk is the estimated position of the tricritical point

On examining the high-temperature magnetic susceptibility curves we see that the mean effective moment tends to 3.6 μ_B, corresponding to a $S = \frac{3}{2}$ ground state with g reduced to 1.86 by spin–orbit coupling. Use of the Abragam and Bleaney formula,[15] an approximation for g, gives a spin–orbit coupling constant of 1600 cm^{-1} for $10Dq = 30\,000$ cm^{-1}. As the temperature is lowered Fig. 1 shows that the magnetic susceptibility along *a* becomes substantially higher than the other two principal values. This is indicative of a zero-field splitting with unique axis along *a*. The susceptibilities between 200 and 300 K can be fitted to give a $2D$ of $-20(2)$ cm^{-1} and an almost isotropic g of 1.86(1).[2] We do not provide a more detailed fitting using lower-temperature data because it is clear that the magnetic exchange interactions are affecting the anisotropy, even at 100 K. These approximate calculations should not be taken to be entirely quantitative, but they do show that we understand the single-ion magnetic behaviour. With $2D \approx -30$ K, the system at lower temperatures can be regarded as an Ising system of moment 2.8 μ_B, with the Ising axis approximately along the crystal *a* axis.

Magnetic exchange. From the structural features of the layered crystal we can predict two-dimensional magnetic coupling in the *bc* plane, with only weak coupling along *a*.

At 1.0 T the magnetic susceptibility plot (Fig. 1) shows antiferromagnetic ordering at 9.7(1) K; $\chi(100)$ is distinctly less than the other susceptibilities below this temperature, indicating that the easy axis, *viz.* the axis of orientation of the moments, is close to being along *a*. However, $\chi(010)$ rises sharply just above the transition, indicating a ferromagnetic interaction along *b*, which causes hidden canting below the transition. When magnetic fields are applied along *a* or *c* nothing unusual happens. For example, at 5 T, the phase transition occurs at 9.5(1) K for $H \| c$ and at 8.7(1) K for $H \| a$. However, when a field is applied along *b* the phase transition is extremely field dependent, as is illustrated in Fig. 5.

This magnetic behaviour is characteristic of a metamagnet. Similar behaviour is observed for [CoL$_2$(NCS)$_2$] (L = triazine)[16] and [CoL$_2$Cl$_2$] (L = urea).[17] In the present case the origin of the metamagnetism is much clearer because of the obvious layer structure. In such a metamagnetic transition the phase boundary between the antiferromagnet and the very highly canted paramagnetic phase is of interest. In particular, we expect the transition to be thermodynamically first order at lower temperatures, but at some tricritical point below the Neel point to become second order. Fig. 3 illustrates that at $T = 5.8(2)$ K and $H = 4.40(5)$ T there does appear to be such a tricritical point. Fig. 5 shows the measured phase boundary above 2 K. The points have been obtained with a variety of step sizes in either field or temperature at various times, so the irregularity of the curve probably reflects the underlying errors in the measurements.

These observations are sufficient to assign with reasonable certainty the low-field space group as $P2_1/c$ and the high-field space group as $Pc2_1n$. The simplest explanation of the magnetic behaviour is that the Re-centred moments lie approximately along *a*, but that there may be small *b*- and *c*-directed components. In the $ReCl_4$ sheets the large *a* component of the moments are ferromagnetically coupled along *b* and antiferromagnetically along *c*/2. At low fields the sheets separated by *a*/2 are antiferromagnetically ordered. As the field is raised at a critical value the magnetic energy gain of flipping the moments of one half of the $ReCl_4$ sheets outbalances the small antiferromagnetic coupling of the $ReCl_4$ sheets along *a*. A transition to a phase with a small net ferromagnetic moment along *b* occurs. We have made the assumption of antiferromagnetic coupling along *c*/2, which is consistent with the data, and provides a *b* moment in the $ReCl_4$ sheets. This small net *b* moment then provides a simple reason for the metamagnetic transition. There is a pair of alternate phases in which one assumes totally ferromagnetic interaction of the *a* components of the moments in the $ReCl_4$ sheets ($P12_1/c1$ and $P2_1cn$). However, this gives an unlikely net high ferromagnetism along *a* for one phase, no obvious choice of phase for low and high field, nor an obvious reason for the transition.

We conclude from this magnetic behaviour that we do have a typical metamagnet. The structures of the magnetic phases are not completely experimentally defined, and thus direct observation by neutron diffraction would be useful. In addition we may hope to gain some information on the distribution of magnetisation over the molecule. It is also clear from, for example, the reduction of spin–orbit coupling constant to 1600 cm^{-1} from the free-ion value of about 3300 cm^{-1} that this complex is substantially covalent in nature.

Neutron diffraction

Unpolarised measurements. We conducted two types of neutron measurements for Bragg reflections, polarised neutron diffraction measurements of flipping ratios, and unpolarised measurements of intensities. The former measures magnetic structure factors accurately, with estimated standard deviations of about 0.01 μ_B per Re. Although dominated by nuclear scattering, the unpolarised data contain a component from magnetic scattering. The accuracy of measurement of this is low here, 1.3 μ_B per Re, partly because of our use of a diffractometer configuration which was optimised for polarised, not unpolarised, measurements.

In the unpolarised measurements we saw no significant magnetic intensity in either allowed or forbidden reflections. Given the total moment per rhenium of 2.8 μ_B, the lack of observed intensity is significant, even allowing for the effect of rhenium positions on phase factors, and the vector-product term in the structure factor between moment and wavevector.[18] We conclude that a substantial proportion of the moment is distributed elsewhere than on the Re atom, such as by covalence onto the ligands. This feature of the magnetisation density reduces the maximum value of the magnetic Bragg intensities which might be observed by a factor of at least four, this being our level of detection.

Even though the magnetic structure factors which are systematically absent in space group *Pccn* are predicted to be small, they may be observable in a further experiment optimised for unpolarised diffraction. This would definitely settle the space group, and define the magnetic structure more completely.

Polarised measurements. The conventional PND experiment involves measurement at Bragg peaks with finite nuclear reflection intensity. Thus we did not measure at *h*0*l* with *l* odd, which are nuclear forbidden. We therefore measured the superposition of the projection on *x*0*z* of the component along *b* of magnetisation density of those pairs of the molecules in the unit cell not related by the inversion symmetry operation. In addition, the flipping ratio of *h*0*l*, *l* even, reflections does change when the magnetisation densities on each of the inversion-related molecules become different. However, this effect is very small, since it does not appear in the nuclear-magnetic interference terms in the flipping ratio. This is because those nuclear structure factors are real quantities and the changing magnetic term is imaginary. Thus, these PND measurements effectively examine the magnetisation density of 1/4 of the unit cell, containing the average magnetisation density of the four molecules in the cell of the *Pccn* structure. Accordingly, our measurements in the *h*0*l* plane cannot answer the question of the relative orientations of the moments on the four molecules in the unit cell, but can give information on the net moments and bonding effects.

Using the program ASRED,[19] the data were fitted by a model in which the spatial distribution of the *b* component of the magnetisation density was modelled as a sum of atom-centred densities. These had radial dependencies of the form of 5d orbitals on Re, 3s on Cl and 2s on C and N.[20] Since the data extend only to $(\sin\theta)/\lambda = 0.32$ Å^{-1} we did not attempt to fit any spatial magnetic anisotropy on the atom sites, because the form factors show that this strongly affects only reflections at higher values of $(\sin\theta)/\lambda$.

Our initial model retained the crystallographic two-fold axis of symmetry along *c* through the rhenium centre in the distribution of the magnetisation measured down the *b* axis. This two-fold axis exists in the *Pccn* nuclear structure. As a benchmark, a model was refined with a spin population only on the Re atom and obtained a goodness of fit, χ^2, 4.95 and $R(F)$, all data, 0.424. The data include the value for reflection 0,0,0 from the bulk-magnetisation experiment. We then refined densities on the Re, Cl(1), Cl(2) and N(1), C(1) and N(2) centres. Significant positive density was obtained on Re and on both chlorine sites, with none on the three amidine ligand atoms N(1), C(1) and N(2); χ^2 was 3.58 and $R(F)$ 0.365. Refining possible density on the phenyl ring produced no significant improvement in fit or appreciable population on the ring.

A distinct improvement in the fit to the data was achieved by removing the two-fold axis of symmetry, which is not required in the magnetic structure. We refined the density on the Re, Cl and N sites, a total of nine parameters (*cf.* 22 observations). This reduced χ^2 to 2.38 and $R(F)$ to 0.255. Addition of refinable populations on carbon atoms, including the amidine carbon C(1), did not improve the fit. The population parameters are given in Table 2.

We notice that only 53(11)% of the total magnetisation is found to reside on the Re, which implies that very substantial covalence is present in the bonding. The remaining magnetisation appears on the ligands. However, there is a complicating factor: there are substantial amounts of a negative *b* component of the magnetisation density. For both chloride and amidine ligands there is a consistent pattern of a large positive density on one ligand matched by a slightly smaller negative density on the site related by two-fold rotation in the nuclear structure. We now see why the removal of this symmetry axis in the magnetic refinement was so important. If this situation is ascribed to a combination of a covalent delocalisation onto both ligands

Table 2 Site magnetisations in the crystal ($\mu_B \times 10^3$) resulting from refinement of the PND data

Re	119(24)		
Cl(1)	65(23)	Cl(1′)	−56(24)
Cl(2)	118(30)	Cl(2′)	−21(18)
N(1)	−18(15)	N(1′)	−3(31)
N(2)	−48(20)	N(2′)	71(25)

plus a dipolar spin polarisation along *a* we obtain a covalent delocalisation of significance only on Cl(2) and Cl(2′) of 42% of the total magnetisation. The prime signifies the two-fold rotation-related atom. The spins on Cl(1), Cl(1′) and the amidine group appear to arise solely by 'polarisation' of the underlying spin-paired orbitals. On each of the three pairs of ligands a 'polarisation' of 27% of the total magnetisation occurs. The situation is complicated by the knowledge that we are only measuring the *b* component of magnetisation, a small component of the total. Thus the 'polarisation' is unlikely to be a magnetisation the scalar product of which with that on the rhenium site is negative, but is more likely to reflect differing orientations of the total moment, which on all sites lies mainly along *a*. If this is true we are observing a combination of covalence, spin polarisation, and a site-dependent canting of the magnetisation away from the magnetic field direction.

A last point is that, as expected, we observe no spin population on the phenyl ring. It is almost orthogonal to the Re−N−C−N amidine fragment, and interactions of π type would be blocked, while those of σ type would be rapidly attenuated by intervening atoms. This orthogonality is probably the main reason for the very weak magnetic exchange pathway along *a*.

Conclusion

The compound $[ReCl_4(NH{=}CMeNHPh)_2]$ is a readily available and chemically robust metamagnet of relatively simple composition. It has the intrinsic interest that the rarity of such behaviour amongst later transition-metal compounds brings. The magnetic exchange pathway within the $ReCl_4$ plane is straightforward, and these planes are well isolated from each other by the layers of phenyl groups. With such simplification available, it may prove a suitable subject for extensive magnetic studies and a deeper theoretical treatment of the magnetic structure relationships than we are able to provide, particularly given the variation provided by phenyl ring substitution.

Acknowledgements

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