The Cyano Nitronyl Nitroxide Radical: Experimental and Theoretical Evidence for the Fourth Case of the McConnell-I Mechanism

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Abstract: The nitronyl nitroxide 2-cyano-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (**1**) crystallises in the tetragonal $P\bar{4}2_1m$ space group with $a = 7.4050(7)$, $c = 8.649(1)$ Å. In the crystal the molecules form layers parallel to the *ab* plane in which they are orthogonal to each other. In the layers there are close contacts, 2.953(2) Å, between the NO groups and the bridging carbon atoms of the O-N-C-N-O fragment of neighbouring radicals. The calculated spin density shows a positive population mainly and equally localised on the NO groups and small but significant negative spin densities on the bridging carbon atom and the cyano nitrogen. Absorption spectra show temperature-dependent transitions related to the magnetic behaviour. The temperature dependence of the magnetic susceptibility in the range 2–300 K reveals that couplings between the radicals are antiferromagnetic, and is interpreted by considering a two-dimensional square array of spin $S = 1/2$ antiferromagnetically coupled ($J = -10$ cm^{-1} and $g = 2.01$). This is interpreted as an exchange coupling through close contact between positive and negative spin densities in orthogonal orbitals on oxygen and carbon atoms, respectively.

Keywords: crystal engineering · exchange coupling · magnetic properties · spin density · supramolecular chemistry

Introduction

Magnetic materials can make for fascinating toys for children and grown-ups, useful devices in high-tech products and intriguing objects for scientific scrutiny.[1] One important goal for this research is magnetically ordered molecular based materials and a key aspect is to understand why intermolecular interactions between open-shell molecules (radicals or paramagnetic metal complexes) are sometimes ferromagnetic and sometimes antiferromagnetic.

McConnell[2] proposed rules based on the unpaired electron densities (spin densities) that allow prediction of the type of magnetic order expected for a given material.[3] Four cases (I–IV) can be distinguished and are schematically outlined in Figure 1. Experimental examples for the first three cases I–III have been found. In this report we present the first evidence for the fourth case.

Case I is the most common. Normally, open-shell molecules interact to give antiferromagnetic coupling and no spontaneous magnetisation.

Case II corresponds to ferromagnetic interactions which are found when the magnetic orbitals (or SOMOs, singly occupied orbitals) are orthogonal, either by design or by accident.

Case III was the main issue of McConnell's letter to the *Journal of Chemical Physics.* He pointed out that ferromagnetic coupling should be the result when: "atoms of positive spin density are exchange coupled most strongly to atoms of negative spin density in neighboring molecules".[2] No such systems existed at that time, but the mechanism has since been experimentally confirmed several times.[3]

Case IV was considered by McConnell as "unlikely", he just noted that then the sign of the magnetic coupling should be reversed (antiferromagnetic). To our knowledge no examples of this fourth possibility have been found to date.

An additional possibility is the charge-transfer (or configuration interaction) mechanism also proposed by McConnell.[4] This is rare, but has occasionally been used to explain the magnetic behaviour in charge transfer salts, for example.[5]

Herein we present the peculiar case of the cyano nitronyl nitroxide radical in which the closest spin–spin contact

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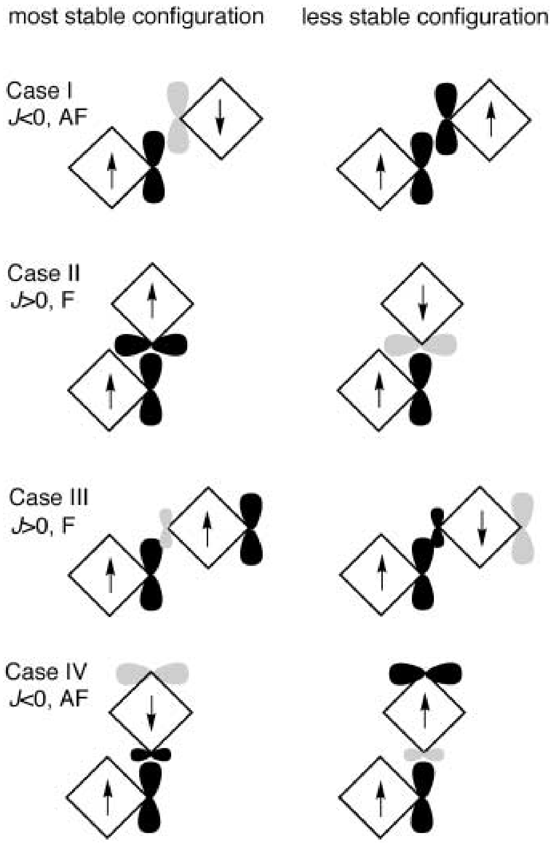

Figure 1. Schematic view of the magnetic couplings according to the McConnell spin density mechanism. Arrows indicate the total spin of each molecular subunit symbolized by a square. Dark and grey "orbitals" denote the positive and negative spin densities, respectively, and smaller "orbitals" illustrate the spin polarization.

between molecules is of the positive–negative type but the exchange coupling is antiferromagnetic, thus a case IV mechanism.

Results and Discussion

X-ray structure: The molecular structure of the cyano nitronyl nitroxide radical (**1**) is shown in Figure 2. The radical **1** crystallises in the tetragonal $P\bar{4}2_1m$ space group and all atoms except the methyl groups (C4) are located in the mirror plane with the cyano group along the two-fold axis. This puts the five-membered ring and the NO groups in the same plane, an unusual arrangement for this type of molecule.[6]

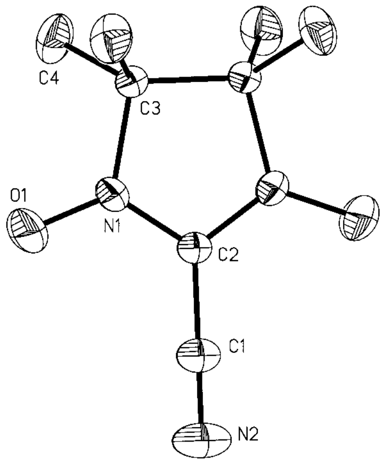

Figure 2. View of the radical **1** with thermal ellipsoid plot at 30% probability level. The hydrogen atoms are omitted for clarity.

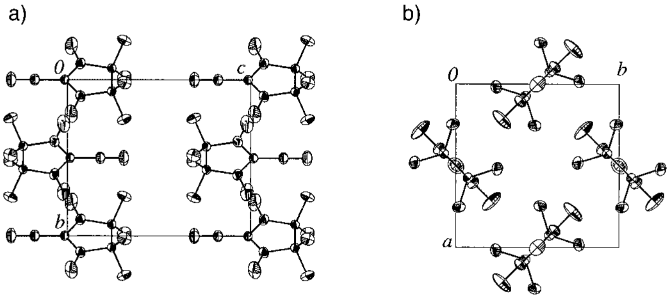

Figure 3. Projection of the crystal structure onto the *bc* (a) and *ab* planes (b).

In the crystal, due to space group symmetries, molecules have their mean plane perpendicular to the *ab* plane (Figure 3b), and make layers parallel to this plane (Figure 3a). In a layer, the radicals are also arranged strictly perpendicular in such a way that they form a two-dimensional (2D) square network (Figure 3b). The oxygen atom O1 of the two NO groups is close to the central carbon C2 (O1–C2 2.953(2) Å) of the neighbouring radicals (Figure 3). The intermolecular distances O1 ··· N1, O1 ··· O1 and N1 ··· N1 between the NO groups are 3.251(2), 3.750(2) and 4.453(2) Å respectively. The shortest intermolecular distances between the layers (Figure 3a) are observed between the cyano nitrogen atoms N1 in one layer and the methyl groups of the nitronyl nitroxide radicals in an adjacent layer (N1 ··· C4 3.490(3)). Selected distances and angles can be found in Table 1.

Magnetism: The temperature dependence of the magnetic susceptibility χ, and its product with the temperature χT are shown in Figure 4. χT is 0.34 $cm^3 K mol^{-1}$ at room temperature, and decreases continuously when cooling and tends to a value close to zero at 2 K, while χ increases to a maximum at 30 K then decreases at lower temperatures. This indicates dominant antiferromagnetic interactions. We simulated the

Table 1. Selected intra- and intermolecular interatomic distances [Å] and angles [°].[a]

O1–N1	1.259(3)	N1–C2	1.330(2)
N1–C3	1.514(3)	N2–C1	1.119(4)
C1–C2	1.416(4)	C3–C4	1.514(2)
C3 ··· C3#1	1.555(5)	O1 ··· C2#3	2.952(2)
O1 ··· N1#3	3.251(2)	O1 ··· O1#3	3.750(2)
N1 ··· N1#3	4.453(2)		
O1-N1-C2	125.7(2)	O1-N1-C3	122.6(2)
C2-N1-C3	111.7(2)	N1-C2-N1#1	111.8(3)
N1-C2-C1	124.1(1)	C4#2-C3-C4	109.4(3)
C4-C3-N1	106.9(2)	C4-C3-C3#1	115.2(1)
N1-C3-C3#1	102.4(1)		

[a] Symmetry transformations: #1: $-x+1, -y+2, z$; #2: $y-1/2, x+1/2, z$; #3: $y-1, -x+1, -z+2$.

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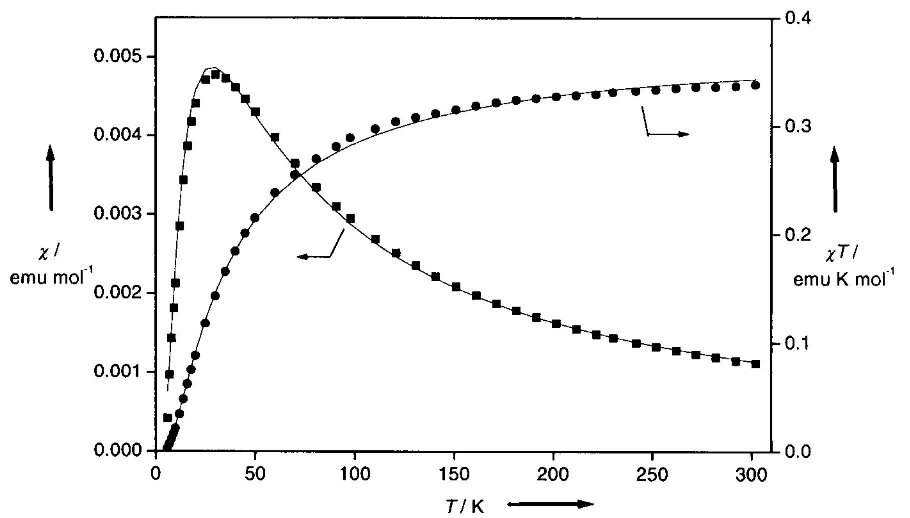

Figure 4. Temperature dependence of the magnetic susceptibility χ and its product with temperature, χT. The solid lines represent the best-fit curves. .

experimental data by using a literature model for a 2D square-planar lattice of antiferromagnetically coupled spins $S = 1/2$.[7] The best fit gave $J = -10\ \mathrm{cm}^{-1}$ and $g = 2.01$.

As mentioned before, the closest spin–spin interaction is between the central carbon atom C2 and the oxygen atom in a neighbouring molecule (O1–C2 2.953(2) Å). Both simple molecular orbital considerations and experimental observations indicate that the spin density on C2 is negative and approximately 5–15% of the positive spin on O1.[8] Furthermore, the consequence of the crystallographic symmetry is to make the p_z orbitals (taking the xy plane as the molecular plane) on C2 and O1 orthogonal in the quantum-chemical sense (overlap = 0). In terms of Figure 1, the radical **1** is clearly a case IV, and the antiferromagnetism thus readily explained.

However, it has been put forward that it may be misleading to take into account only the shortest spin–spin interaction.[9] It may thus be argued that the larger spin densities on neighbouring O and N atoms may make up for the longer distance (O1–N1 3.251(2)) and play a role in determining the overall magnetic interaction.

To prove the "case IV" mechanism we would have to grow crystals of a different phase with the radicals **1** slightly tilted, in order to break the orthogonality, but retaining the C2–O1 interaction as the closest spin–spin contact. The system should then revert to a "case III" ferromagnetic coupling similar to that found in, for example, 5-pyrimidinyl-nitronyl nitroxide.[10]

Density functional theory calculations: An experiment such as that mentioned above could only be carried out with the help of a good portion of luck and a lot of patience. However, a second best possibility was available, density functional theory calculations. We chose a three-radical system (see Figure 5) where we first calculated the magnetic coupling for a system with the X-ray geometry to $J = -25\ \mathrm{cm}^{-1}$, a reasonable agreement with the experimental value ($-10\ \mathrm{cm}^{-1}$) considering the differences between the model system and the real system. The two peripheral radicals were then rotated 10° around the C_2 axis and a new J value calculated. This time, when the orthogonality between the p_z orbitals on C2 and O1 had been broken, a change of sign occurred. The new J value was calculated to be $+3\ \mathrm{cm}^{-1}$, thus a ferromagnetic coupling. This is just as predicted if the C2–O1 interaction is the dominant factor. Indeed, there seems to be no other way to account for the calculated ferromagnetism in the tilted model system.

Moreover, a spin density plot (Figure 6) shows normal behaviour of the spin densities, and population analysis gives the spin populations at N1, O2 and C1 as +0.23, +0.32 and −0.09, respectively. The cyano unit has the spin populations C2 = +0.01 and N2 = −0.03.

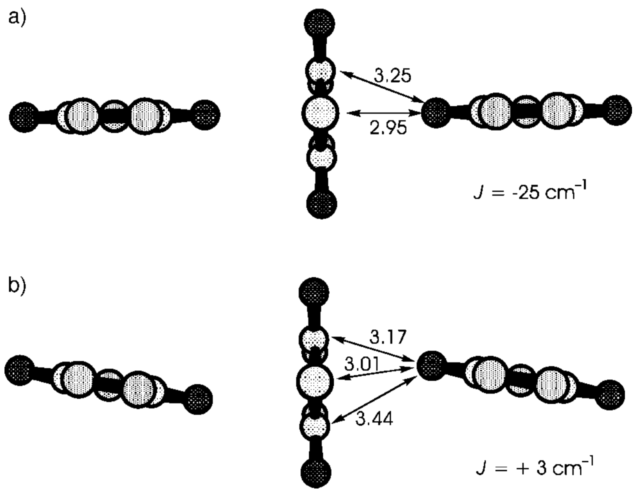

Figure 5. The three-radical system used as a model for calculating the magnetic coupling. a) the X-ray geometry and b) a model with the terminal radicals rotated 10° around the N2-C1-C2 axis. Hydrogen atoms omitted for clarity. Distances between O1–C2 and O1–N1 are indicated.

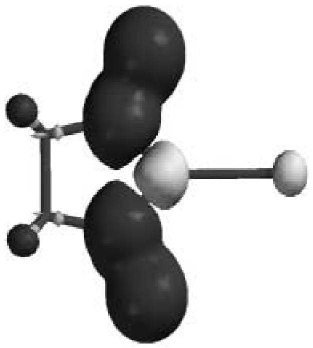

Figure 6. Calculated spin density (X-ray geometry). black: positive, white: negative, boundaries ±0.002 e⁻.

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Absorption spectra: Following the discovery of the unique magnetic properties of the title compound, we measured low-temperature single-crystal absorption spectra, a technique that has been shown to lead to complementary insight on magnetic properties.[11] Single-crystal absorption spectra are shown in Figure 7. The overall spectra between 13000 cm^{-1} and 20000 cm^{-1} (750–500 nm) in Figure 7a show the two lowest energy electronic band systems, which both have rich vibronic structure, and are similar to other nitronyl nitroxides and their metal complexes.[12] The structure of the spectra is well resolved. We will focus on the series of transitions of which one representative is denoted by the vertical arrow in Figure 7a. In contrast to all reported spectra of nitronyl nitroxides, the lowest energy band system, to which all transitions below 15000 cm^{-1} belong, contains a number of sharp transitions with widths of approximately 6 cm^{-1}, indicated by the vertical arrows in Figure 7b. These transitions show a striking temperature dependence: their intensity decreases very rapidly between 5 and 20 K, distinctly different from the other bands, which correspond to intramolecular vibronic bands.

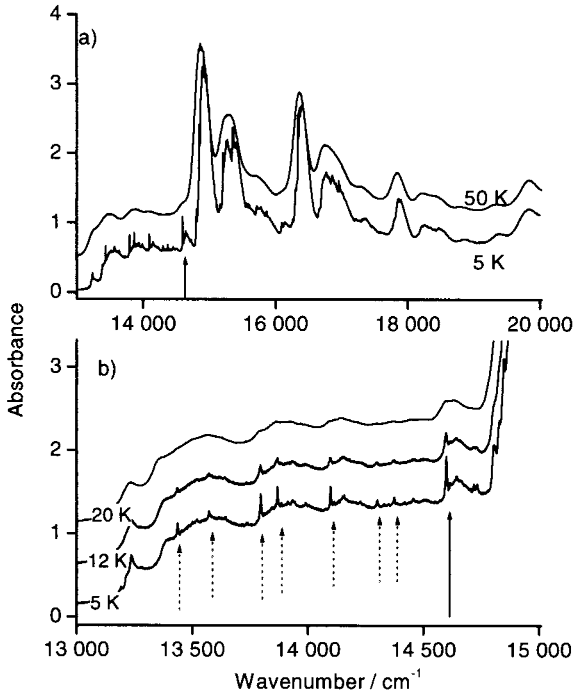

Figure 7. Low-temperature absorption spectra of crystalline **1**. a) Overall Vis spectra. b) Detailed view of the lowest energy electronic transition. The arrows denote bands whose intensity varies with the magnetic order, as illustrated in Figure 8.

Both the narrow width and the temperature dependence indicate that these bands are most likely cooperative transitions occurring only in the antiferromagnetically ordered phase and therefore give us a complementary experimental approach to monitor the magnetic behaviour.

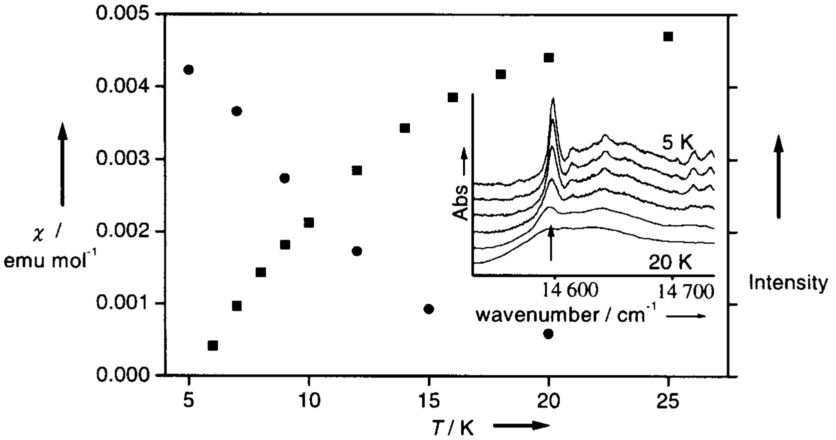

Figure 8. Temperature dependence of the intensity of the absorption band denoted by the solid arrow in Figure 7 and in the inset (circles) compared to the magnetic susceptibility (squares). The inset shows the detailed temperature dependence of the absorption band denoted by the solid arrow in Figure 7.

The temperature dependence between 2 and 20 K is given for the transition denoted by the solid arrow in the inset to Figure 8. It is identical to the temperature dependence for all transitions marked by arrows in Figure 7. Figure 8 compares the temperature dependence of the integrated absorptivity with the change of the magnetic susceptibilty χ. It is evident that the magnetic behaviour is mirrored by the absorption intensity, underlining the nature of these transitions as cooperative bands specific to the magnetically ordered phase. However, we do not attempt to quantitatively determine the exchange parameter from the absorption intensities since we ignore the underlying mechanisms and the splitting pattern of the bands denoted by arrows in Figure 7 is too complex to be analyzed by literature models.[11]

Absorption transitions mirroring the magnetic order in two-dimensional antiferromagnets have been reported for transition metal halides such as $NiCl_2$ and $NiBr_2$,[13] but this is to our knowledge the first report of such bands for an organic solid. The number of observed bands associated with the magnetically ordered phase is much higher than for the transition metal systems. Such bands have not been observed for any other nitronyl nitroxide system that we have studied by single-crystal spectroscopy, underlining the unique character of the magnetically ordered phase of the title compound.

Conclusion

Structural, magnetic, spectroscopic and quantum-chemical evidence suggests that the cyano nitronyl nitroxide radical is an example of magnetic coupling through polarized spin densities not encountered before: antiferromagnetic coupling by close contact between positive and negative spin densities in orthogonal orbitals.

Experimental Section

Syntheses: All reagents were purchased from commercial sources and used without further purification. 2,3-bis(hydroxylamino)-2,3-dimethylbutane, and 2-bromo-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide, were prepared according to literature methods.[14]

2-Cyano-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (1): This compound was synthesised by a slight modification of a literature method.[15] Freshly synthesised 2-bromo-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (1 g) was crushed with dry NaCN (2.2 g). The mixture was suspended in dry DMF (4 mL) and heated at 50 °C. After 30 min the reaction was stopped. Then water (10 mL) and dichloromethane (25 mL) were successively added. The radical was extracted from the reaction mixture with dichloromethane (5×20 mL) and was purified by silica gel column chromatography with a mixture of dichloromethane and n-pentane (70/30) to give **1** (300 mg; 38 % yield). M.p. 149 °C; elemental analysis calcd for $C_8H_{12}N_3O_2$: C 52.74, H 6.64, N 23.06, O 17.56; found: C 52.56, H 6.62, N 22.97, O 17.64.

X-ray crystallography: Data were collected at room temperature (300 K) with a Bruker SMART CCD diffractometer equipped with a normal focus molybdenum-target X-ray tube. The data were processed through the SAINT data reduction and absorption correction software.[16] The structure was solved and refined on F^2 using the SHELXTL software.[17] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in the final refinement model in calculated position with isotropic thermal parameters

Crystallographic data for **1**: Crystal dimensions: $0.2 \times 0.2 \times 0.2$ (mm), $\lambda = 0.71060$ Å; $M_r = 182.21$, tetragonal, space group $P\bar{4}2_1m$ (no. 113), $a = 7.4050(7)$, $c = 8.649(1)$ Å, $V = 474.27(9)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.276$ g cm^{-3}, $F(000) = 194$, 52 parameters; $R(F) = 0.0490$ ($wR(F^2) = 0.1500$, GOF = 1.155) for all 645 data ($I > 2\sigma(I)$); min./max. residual electron density: $-0.174/0.190$ e Å^{-3}, $\mu = 0.724$ cm^{-1}; 1878 reflections collected, $2\theta_{max} = 59°$. CCDC-175914 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

Computational details: All calculations were made with DGauss[18] by employing the exchange and correlation functionals of Becke[19] and Perdew,[20] respectively (BP86), and a DZVP basis set.[21] Calculation of the magnetic couplings were performed by using the broken symmetry formalism on a linear three-radical model with all methyl groups replaced by hydrogen atoms using 1) the X-ray geometry and 2) a model with the terminal radicals rotated 10° around the N2-C1-C2 axis in order to break the orthogonality. The resulting energy differences have to be corrected since the $\alpha\beta\alpha$ states are not exact spin states, they are referred to as broken symmetry states. Thus while the energy difference between the true doublet and the quartet can be calculated to $3J$,[3] the corresponding energy difference between the $\alpha\beta\alpha$ and $\alpha\alpha\alpha$ states can be calculated to $2J$.[22] The spin density of a single radical **1** was calculated by using the complete X-ray geometry.

Magnetic susceptibility measurements: The magnetic susceptibilities were measured on the bulk materials in the 2–300 K temperature range with a Quantum Design MPMS superconducting SQUID magnetometer operating at a field strength of 0.5 T. The data were corrected for diamagnetism of the constituent atoms using Pascal constants.

Absorption spectroscopy: Absorption spectra were measured on a Varian Cary5E spectrometer using the photomultiplier tube detector for the visible range. The sample crystals was cooled in a He gas flow cryostat (Oxford Instruments CF1204) and the temperature was monitored with a RhFe resistor connected to an electronic controller (Oxford Instruments ITC4) to stabilise the temperature by adjusting both a heater for the He gas cooling the sample and the gas flow valve from the He storage dewar to the cryostat. This system allows us to stabilise the temperature to the precision of better than 1 K needed for this project. All spectra presented in the following are unpolarised, as no strong dichroic effects were observed in preliminary spectra polarised along the optical extinction directions of sample crystals.

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