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Date:
2020-04-16

Citation:
Hudson, T. A., Sutton, A. L., Abrahams, B. F., D'Alessandro, D. M., Davies, C. G., Goerigk, L., Jameson, G. N. L., Moubaraki, B., Murray, K. S., Robson, R., Usov, P. M. & Yang, G. (2020). A Semiconducting Cationic Square-Grid Network with FeIII Centers Displaying Unusual Dynamic Behavior. European Journal of Inorganic Chemistry, 2020 (14), pp.1255-1259. https://doi.org/10.1002/ejic.202000130.

Persistent Link:
https://hdl.handle.net/11343/275545

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To be cited as: 10.1002/ejic.202000130

Link to VoR: https://doi.org/10.1002/ejic.202000130

A Semiconducting Cationic Square-Grid Network with Fe(III) Centers Displaying Unusual Dynamic Behaviour

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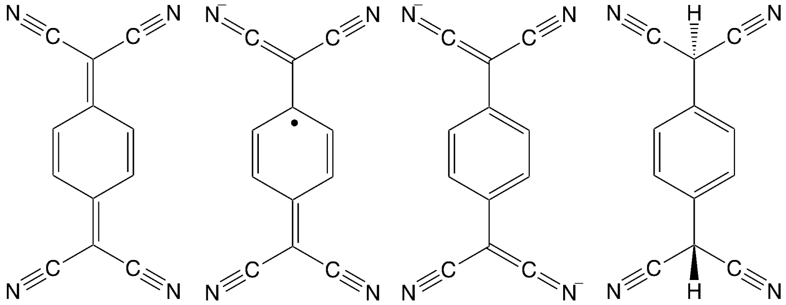
*Supporting Information can be found under https://doi.org/10.1002/chem.2020*****

Abstract

The synthesis, structure and properties of a 2D Fe(III) network material of composition [Fe(O-bipy)$_2$Cl](TCNQ)$_2$ (O-bipy = 4,4'-bipyridyl N,N'-dioxide); TCNQ = 7,7,8,8-tetracyanoquinodimethane**)** are presented. The structure consists of a square grid in which square pyramidal Fe(III) centers are linked to four equivalent centers through O-bipy ligands. Pairs of TCNQ radical anions are located within rectangular cavities of the 2D network. The apical position on each Fe center is occupied by a chloride ion. Magnetic studies are indicative of weak antiferromagnetic coupling. Electrical conductivity measurements reveal that the compound is a semiconductor and on the basis of DFT calculations it is proposed that electrical conduction occurs via charge hopping between interlayer TCNQ anions. Mössbauer spectra indicate a rare example of the Goldanskii-Karyagin effect and are suggestive of unusual dynamic processes.

Interest in coordination polymers has grown substantially over the last 30 years and continues to attract considerable attention not only in the synthesis and structure of network materials but also with respect to applications. The ability to tune framework properties through judicious choice of metal centers and/or ligands has underpinned much of this growth. To date, the emphasis has been on frameworks that exhibit porosity and thus many applications lie in the area of gas storage and separation.[1-4] The investigation of the electronic properties of coordination polymers is not as advanced, although it is attracting increasing attention as it may lead to significant advances in the areas of energy storage, sensors, and electrocatalysis.[5]

Over several years a particular focus of our work has been the generation of networks in which redox-active ligands bridge metal centers.[6] 7,7,8,8-Tetracyanoquinodimethane, TCNQ, is an ideal candidate in such endeavours with three readily accessible oxidation states and, potentially, four N-donor atoms located at the vertices of a rectangle. The neutral form (I) is a strong acceptor, which can undergo a one electron reduction to yield the stable radical anion, $TCNQ^{\cdot-}$ (II). Structures of metal-$TCNQ^{\cdot-}$ network materials have been characterised and shown to exhibit interesting electronic and magnetic properties.[7] A further one electron reduction results in the generation of the moderately air sensitive dianion, $TCNQ^{2-}$ (III). We have found the protonated form of $TCNQ^{2-}$, $TCNQH_2$ (IV), to be a stable and convenient precursor in the synthesis of a wide variety of crystalline dianionic TCNQ coordination frameworks in which metal centers are linked by $TCNQ^{2-}$.[8,9]



Rigid linear bridging ligands such as 4,4’-bipyridine (4,4’-bipy) are commonly employed co-ligands for the formation of multidimensional frameworks. The closely related species, 4,4'-bipyridyl N,N'-dioxide (O-bipy), has been exploited also as a bridging ligand in numerous coordination materials although not to the same extent as 4,4'-bipy.[10,11] The 3D framework $[Zn_2(TCNQ)_2(CH_3OH)_2(O\text{-bipy})]$ comprised of Zn-TCNQ sheets, bridged by O-bipy ligands, was prepared using the $TCNQH_2$ approach.[9] As part of our investigations of TCNQ coordination polymers we were interested in generating network materials in which Fe-TCNQ sheets are linked by O-bipy ligands. The synthetic approach employed resulted in the unexpected generation of $TCNQ^{\cdot-}$ radicals which were found to serve as uncoordinated counteranions for a cationic square grid network. The serendipitous synthesis and characterisation of this unusual material is described below.

Slow diffusion of a methanolic solution of O-bipy into a solution of iron(II) chloride and $TCNQH_2$ in N,N-dimethylformamide (DMF), yields dark purple crystals over several days. The crystals were found to have the composition, $[Fe(O\text{-}bipy)_2Cl](TCNQ)_2$. Presumably the generation of Fe(III) is due to aerial oxidation. The compound may also be generated by using iron(III) chloride as a starting material however neutral TCNQ is a co-precipitate in these reaction mixtures. The homogeneous product obtained from the mixture containing $FeCl_2$ was used in the examination of physical properties. Herein, we describe the structure, magnetism, spectroscopic properties and electrical conductivity of this unusual crystalline material.

Each of the Fe(III) centers is in a square pyramidal coordination environment formed from a chloride ion, which occupies the apical site, and four symmetry-related oxygen atoms, each belonging to an O-bipy ligand that forms a bridge to a symmetry-related Fe(III) center. With each Fe(III) linking to four equivalent centers through bridging O-bipy ligands, a cationic square grid network of composition $[Fe(O\text{-}bipy)_2Cl]^{2+}$, is generated (Figure 1a). The oxygen and nitrogen atoms of the O-bipy ligands lie on a crystallographic mirror plane which coincides with the mean plane of the network. The square pyramidal Fe(III) centers are disordered over a pair of symmetry related positions, sitting above and below the mean plane of the sheet. With a bend at each donor O atom the Fe(III) centers bound to a single O-bipy are located on the same side of the O-bipy ligand. As a result, the sheet possesses rectangular $Fe_4(O\text{-}bipy)_4$ cavities (~9.4 x 14.2 Å) that alternate in orientation in a chequered manner within a sheet. A pair of symmetry related monoanionic TCNQ molecules, which form a perfectly aligned dimer, occupy the rectangular space, corralled by the O-bipy ligands as indicated in Figure 1a. Bond lengths in TCNQ are sensitive to the oxidation state and using the empirical Kistenmacher relationship, it is possible to estimate the charge on the TCNQ (see Supporting Information).[12,13] Using this relationship, the charge on the TCNQ species is calculated to be -1.27(17).

Each $TCNQ^{\cdot-}$ unit participates in face-to-face π-π interactions with its symmetry-related partner with a centroid to centroid separation of 3.25 Å. In addition to the close contact between the $TCNQ^{\cdot-}$ units, the separation between the mean planes of the $TCNQ^{\cdot-}$ and the adjacent O-bipy ligand is 3.27 Å. Close edge-to-face interactions between the $C(CN)_2$ edge of the $TCNQ^{\cdot-}$ anion and the bridging O-bipy ligand are also apparent, with the closest contact between the cyano carbon of the $TCNQ^{\cdot-}$ and the α-carbon of the O-bipy ligand being 3.21 Å. A space filling representation (Figure 1b) clearly shows the snug fit of the $TCNQ^{\cdot-}$ dimer within each Fe_4(O-bipy)$_4$ rectangular cavity. The complementary arrangement of the TCNQ dimers within the rectangular cavities of the $[Fe(O\text{-}bipy)_2Cl]^{2+}$ network would seem to be a significant driving force for the formation of this particular structure. Whilst the Fe(III) centers in adjacent sheets are aligned in a direction perpendicular to the mean plane of the network, the sheets stack in an ABAB fashion in which the Fe_4(O-bipy)$_4$ rectangular spaces alternate in orientation when viewed normal to the plane of the 2D network. In projection, the orientation of TCNQ dimers resembles a ‘tic-tac-toe’-like grid (Figure 1c).

Mössbauer spectroscopy was employed to confirm the oxidation state of the Fe centers and provide support for the magnetic data below. ^{57}Fe Mössbauer spectra were collected between 5.4 K and 293 K. Above 20 K an asymmetric quadrupole doublet was observed with parameters consistent with high spin Fe(III) that converted into a mixture of fast and slow relaxing subspectra at very low temperatures (< 20 K) (Figure S3.1, Supporting Information). Above 20 K the quadrupole doublet has a quadrupole splitting that is unaffected by temperature (ΔE_Q = 0.55 mm s^{-1}, Table S3.1, Supporting Information). However, the isomer shift is temperature dependent due to the second order Doppler effect.

This dependence can be fitted to a Debye model describing the ^{57}Fe atom with its surroundings atoms (M_{eff}) vibrating with a corresponding Debye temperature that is the Mössbauer temperature Θ_M (see Figure S3.2, Supporting Information). From the best fit, M_{eff} = 93 and Θ_M = 190 K which suggests that the Fe-Cl unit is the mass involved in recoil-free absorption. The data and fit are shown in Figure 2 and the Supporting Information (Figure S3.1).

As the temperature is raised the symmetric quadrupole doublet becomes more asymmetric, without significant line broadening. When this effect is temperature dependent it strongly suggests that crystal anisotropy causes the Mössbauer transition to be directionally dependent. This was first described experimentally and theoretically by Goldanskii and Karyagin and is known as the Goldanskii-Karyagin effect.[14,15] This effect, which is more prevalent in ^{119}Sn compounds,[16] has been reported for complexes such as $[Fe(salen)Cl]_2$ (salen = N,N'-ethylenebis(salicylimine).[17] The asymmetry in the intensities (I_2/I_1, Figure 2) of a quadrupole split spectrum is caused by an anisotropic Lamb-Mössbauer factor (*f*) (see Supporting

Information) and can be fitted to an axial change in the nuclear displacement (Figure 2, inset). The temperature dependence of the anisotropic Lamb-Mössbauer factor is almost certainly due to the structural features of the cationic network itself. Given that the square pyramidal Fe center lies on a grid with a chlorine atom in the apical position, an axially dependent Lamb-Mössbauer factor may be expected and this appears to be the case.

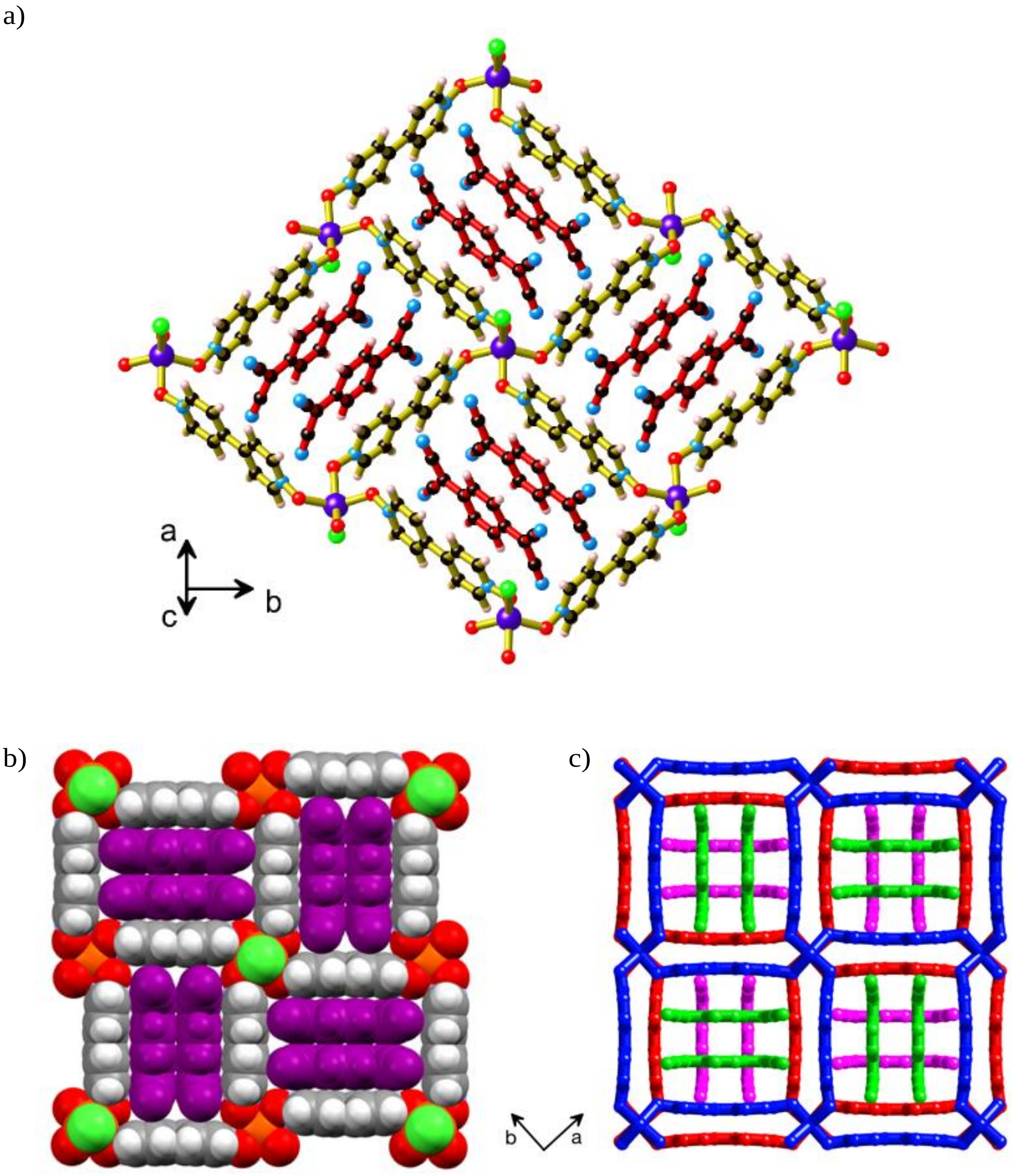


Figure 1. The structure of [Fe(O-bipy)$_2$Cl](TCNQ)$_2$ showing a) a single [Fe(O-bipy)$_2$Cl]$^{2+}$ network with TCNQ monoanions located in the rectangular cavities; Fe purple, Cl green, O red, N light blue, C black, H pink b) a space-filling representation of a single network with the TCNQ dianions viewed

along the *c*-direction; framework atoms: Fe orange, Cl green, O red, C grey, H light grey, TCNQ atoms purple c) a stick representation of the structure viewed along the *c*-axis showing a pair of networks (blue-front, and red-back) and the two different orientations of the TCNQ dianions (green and pink) in the rectangular cavities.

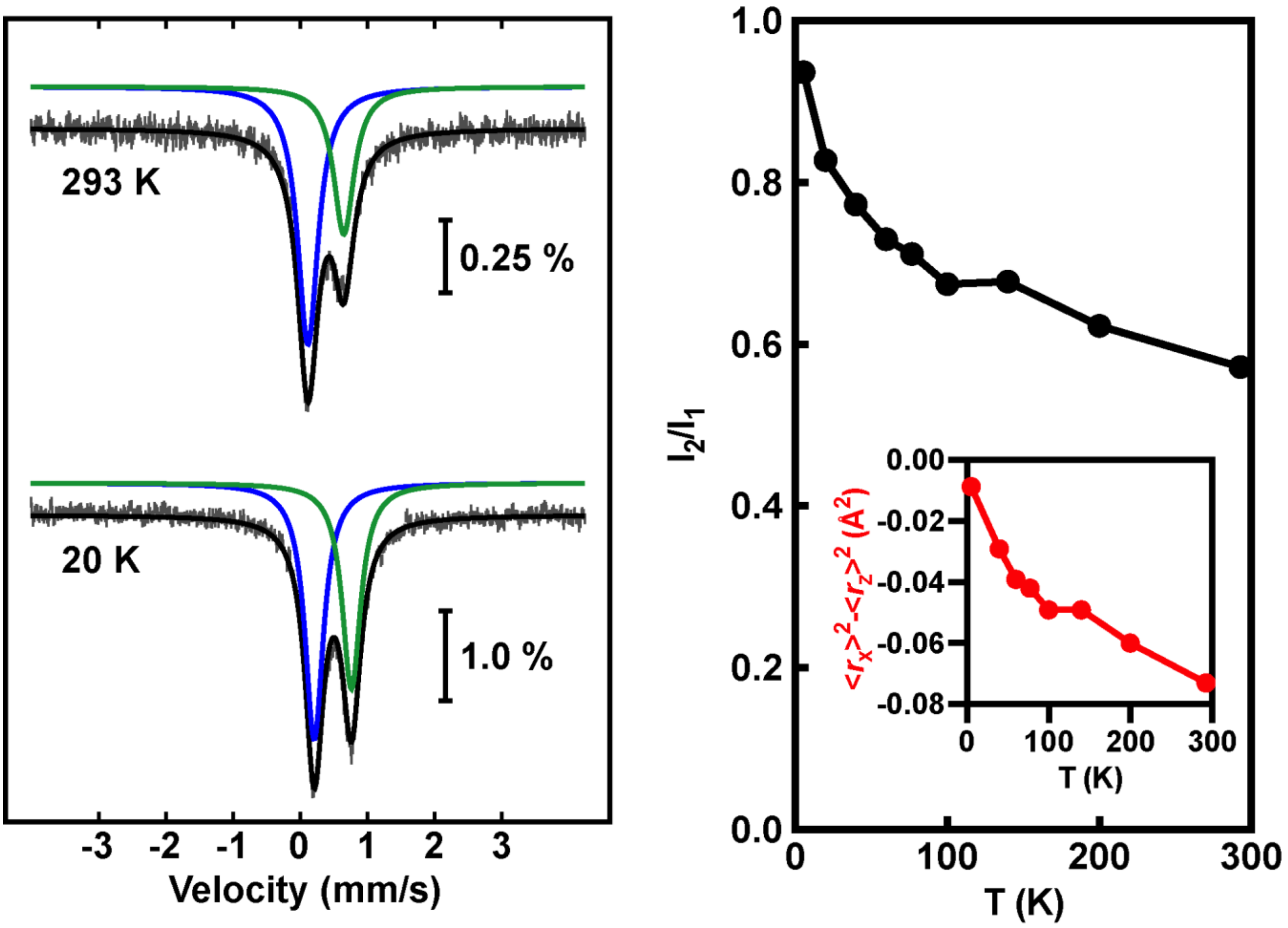


Figure 2. Left: ^{57}Fe Mössbauer spectra of [Fe^{III}(O-bipy)$_2$Cl](TCNQ)$_2$. The quadrupole doublet can be fitted to two Lorentzian peaks of equal width but differing intensity (blue and green). Right: The difference in intensities (I_2/I_1) can be fitted to a change in nuclear displacement ($<r_x>^2-<r_z>^2$) over a wide temperature range.

The temperature dependence of the asymmetry in the Mössbauer spectra prompted a closer examination of the structure, in particular the thermal displacement parameters of the Fe and Cl centers, to determine whether significant dynamic processes occur within the crystal. It was found that the thermal ellipsoids for the disordered Fe(III) center begin to overlap when represented at the 90% probability level (Figure S4.1(c), Supporting Information). This is consistent with the Fe center shuttling from one side of the 2D network to the other. Fourier difference maps in which the Fe and Cl atoms have not been assigned also show distributions of electron density that support this dynamic process (Figure S4.2, Supporting Information).

The movement of an Fe center from one side of the sheet to the other raises the question of whether this occurs as an isolated event or is in fact part of a concerted movement of Fe atoms throughout the crystal. If the movement of Fe centers is a localised process, the breakage of Fe-Cl bonds on one side and the formation on the other would result in chloride ions existing both as μ_2 bridging ligands and uncoordinated anions. The alternative is a concerted movement of Fe centers along a direction parallel with the *c*-axis. Such a process in which the Fe centers shuttle, in unison, between two symmetry related sites, as depicted in Figure 3, would certainly be remarkable. Further investigations of the dynamic processes within [Fe(O-bipy)$_2$Cl](TCNQ)$_2$ are currently underway.

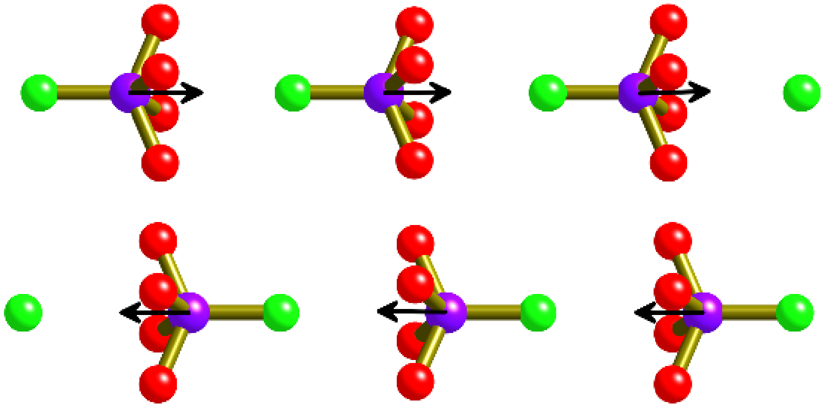


Figure 3. Representations of the coordination environments of the Fe centers (purple) showing two distinct orientations, (a) and (b), of the square pyramidal geometry. In a concerted shuttling process the Fe centers would move, in unison, back and forth along a direction parallel to the horizontal *c* axis, between symmetry-related sites on either side of the [Fe(O-bipy)$_2$Cl]$^{2+}$ framework.

A vibrational spectroscopic analysis was undertaken to confirm the oxidation state of the TCNQ units. The infrared spectrum of [Fe(O-bipy)$_2$Cl](TCNQ)$_2$ shows two ν(CN) stretches at 2187 and 2161 cm^{-1} which are indicative of the radical anionic state for TCNQ.[18] The Raman spectrum contains several vibrational bands which are sensitive to the laser excitation energies. Raman spectra recorded at three different wavelengths are presented in Figure S8.1 (Supporting Information). Bands corresponding to CN vibrations were located at 2198, 2212 cm^{-1} (514 nm); 2161, 2198 cm^{-1} (633 nm) and 2198 cm^{-1} (785 nm); laser wavelengths are indicated in parentheses. These peaks closely match those of previously reported CT complexes containing TCNQ radical dimers.[19] The Raman vibrational peak at 1388 cm^{-1}, which is independent of laser wavelength, is consistent with TCNQ in its monoanionic form.[20]

The TCNQ$^{\cdot-}$ anions within the cationic rectangular cavities exist as diamagnetic dimers and subsequently do not produce an EPR signal. The EPR spectrum of [Fe(O-bipy)$_2$Cl](TCNQ)$_2$ (Figure

S10.1) shows a very weak signal consistent with TCNQ$^{\cdot-}$ not being 100% coupled. In contrast uncoupled TCNQ$^{\cdot-}$ radicals yield an intense EPR signal.[13] No signals corresponding to Fe(III) were apparent, presumably as a consequence of fast relaxation.

A plot of molar susceptibility vs temperature, per Fe, shown in Figure 4 shows a maximum at 7.0 K indicative of weak antiferromagnetic coupling. The existence of any long-range magnetic order would need AC susceptibilities to be probed. The non-zero values of χ_M below 7 K suggests possible inclusion of Curie-like impurities. Indeed, as indicated above, the EPR spectrum of the same sample, showed a weak radical species (g = 2.0022) indicative of traces of non-dimer TCNQ$^{\cdot-}$. The corresponding plot of $\chi_M T$ vs. T, in a field of 1 T, (Figure S11.1, Supporting Information) shows $\chi_M T$ to be 4.0 cm^3 mol^{-1} K at 300 K, slightly lower than the high spin Fe(III) value of 4.4 cm^3 mol^{-1} K. It decreases very little down to ~70 K, then rapidly towards zero at 2 K. Each pair of TCNQ radical anions is strongly antiferromagnetically coupled and is expected to be diamagnetic. Fitting of the data to a 2D S = 5/2 model[21] yielded best-fit parameters of g = 1.92, J = -0.26 cm^{-1}, the very small J being due to coupling across the long O-bipy bridges.

Crystals of [Fe(O-bipy)$_2$Cl](TCNQ)$_2$ possess a purple metallic sheen, commonly observed in radical anionic TCNQ charge-transfer complexes. The UV-Vis-NIR spectrum (see Supporting Information) shows an intense absorption in the region 15000-20000 cm^{-1}, consistent with reported assignments for the TCNQ$^{\cdot-}$ dimer.[22] Tauc analysis allowed an estimate of the optical bandgap of *ca.* 1.0 eV, which suggests the compound should exhibit semi-conductivity. Pressed pellet conductivity measurements using a four-point probe setup revealed a conductivity of 4.4 x 10^{-5} S cm^{-1} at room temperature. The thermal variation (210 – 300 K) of the electrical conductivity showed typical semiconductor behaviour (Figure 5), with an activation energy (E_a) of 0.21 eV, as calculated from the Arrhenius equation (see Figure 5 inset).

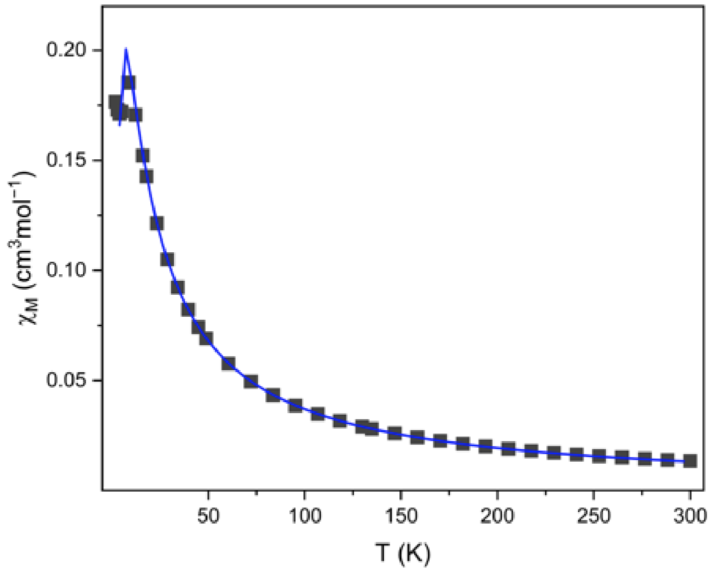


Figure 4. Plot of χ_M versus temperature for [Fe(O-bipy)$_2$Cl](TCNQ)$_2$ The solid line is the best fit using a $S = 5/2$ 2D model described in the text.

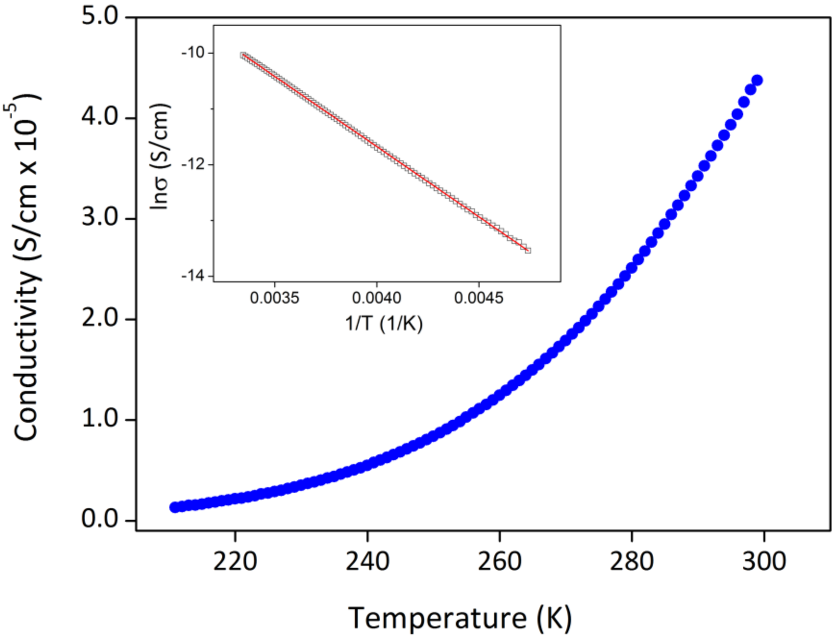


Figure 5. Temperature dependence of conductivity for a pressed pellet of [Fe(O-bipy)$_2$Cl](TCNQ)$_2$ measured using a four point-probe setup. Inset: Arrhenius plot of the conductivity (the red line shows the linear fit).

Solid-state density functional theory (DFT) calculations were undertaken to aid in understanding the electronic structure and mechanisms for electrical conduction through the framework. The band structure and density of states plot are presented in Figure S12.1 and S12.2 (Supporting Information), along with details relating to the calculations. The calculations at the HSE06[23]//PBE[24]-D3(BJ)[25] level of theory provided an estimated bandgap of 0.97 eV, which is in good agreement with experimental measurements. Carbon and nitrogen *p* orbitals belonging to the TCNQ monoanions are major contributors to the valence and conduction bands as indicated in Figures S12.2 and S12.3 (Supporting Information). The high spin Fe(III) center is also involved in the spin-down conduction band but its contribution is relatively minor. The valence and conduction bands are both very flat with bandwidths of less than 10 and 30 meV respectively. Given the dominant contribution of C and N TCNQ *p* orbitals to both the conduction and valence bands it is proposed that the electrical conductivity occurs via charge hopping transport between interlayer TCNQ anions arranged in an edge-to-edge manner.

In conclusion, the structure and properties of an unusual cationic coordination polymer have been described in which the role of the non-coordinated counteranion is played by the TCNQ radical. The crystal structure reveals an aesthetically pleasing complementarity between the rectangular corrals provided by the bridging O-bipy ligands and the $TCNQ^{\cdot-}$ dimer. Over many decades there have been numerous attempts to synthesise TCNQ-based materials in which the combination of discrete electron deficient and electron rich species gives rise to structural arrangements that result in semiconducting or even conducting crystals. With the generation of the square grid coordination polymer in this current work, a novel arrangement of $TCNQ^{\cdot-}$ dimers has been achieved. The work offers the prospect of exploiting spaces within charged frameworks to place redox-active and radical species in novel arrangements which in turn may lead to materials with unusual electrical properties. Furthermore, the use of a network which itself is redox-active, offers scope for the interplay of redox processes between framework and counterion. The electrical and magnetic properties of such materials would be well worth investigating. Finally, Mössbauer and structural studies on $[Fe(O\text{-}bipy)_2Cl](TCNQ)_2$ suggest unusual dynamic processes are occurring that warrant further investigation.

Experimental Section

Synthetic details are presented in section S1 of the Supporting Information.

Crystal data for $[Fe(C_{10}H_8O_2)_2Cl](C_{12}H_4N_4)_2$, $C_{44}H_{24}N_8O_4ClFe$, $M = 876.05$, tetragonal, $a = 17.2282(3)$, $c = 12.8629(5)$ Å $U = 3817.8(2)$ Å^3, $T = 100.0(1)$ K, space group $I4/mcm$ (no.140), $Z = 4$, 6505 reflections measured, 1109 unique ($R_{\text{int}} = 0.0420$), which were used in all calculations. The final $wR(F^2)$ was 0.2706 (all data) and $R1$ ($I > 2\sigma(I)$) was 0.0835. Deposition Number 1939297 contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Acknowledgments

The authors thank Dr Stephen Best for helpful advice regarding EPR. The support of the Australian Research Council is gratefully acknowledged. ALS thanks the Australian Government for an Australian Postgraduate Award. This research was undertaken with the assistance of resources and services from the National Computational Infrastructure (NCI), within the National Computational Merit Allocation Scheme (project fk5). Part of this work was undertaken on the Powder Diffraction Beamline at the Australian Synchrotron.

Keywords: coordination polymer · conductivity · Goldanskii-Karyagin effect · magnetism · TCNQ

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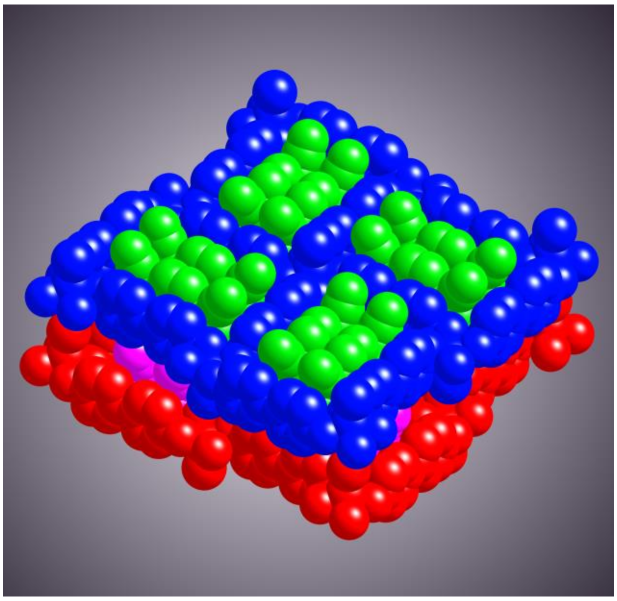

Cationic Networks

The synthesis, structure and properties of a 2D Fe(III) network material of composition $[Fe(O\text{-}bipy)_2Cl](TCNQ)_2$ (O-bipy = 4,4'-bipyridyl N,N'-dioxide); TCNQ = 7,7,8,8-tetracyanoquinodimethane) is presented. Electrical conductivity measurements, consistent with DFT calculations, reveal that the compound is a semiconductor. Mössbauer spectra indicate a rare example of the Goldanskii-Karyagin effect and are suggestive of unusual dynamic processes.