X-Ray diffraction and magnetic studies on a series of isostructural divalent metal chloranilates with zigzag polymeric chain structures and on a dinuclear iron(III) chloranilate †

Brendan F. Abrahams,[a] Kevin D. Lu,[b] Boujemaa Moubaraki,[b] Keith S. Murray[b] and Richard Robson *[a]

[a] School of Chemistry, University of Melbourne, Parkville, Victoria, 3052, Australia
[b] Department of Chemistry, Monash University, Wellington Road, Clayton, Victoria, 3168, Australia

The reaction of iron(III) ion with chloranilic acid (2,5-dichloro-3,6-dihydroxycyclohexa-2,5-diene-1,4-dione) in hot aqueous solution in air generated a product in which the iron, surprisingly, is in the +II oxidation state as is indicated by structural, magnetic and Mössbauer spectral studies. Single crystal X-ray studies of the product of composition $[Fe(C_6Cl_2O_4)(H_2O)_2]\cdot H_2O$ reveal a 1-dimensional zigzag polymeric structure with iron(II) ions carrying two *cis* water ligands linked together by bridging chloranilate anions. Hydrogen bonding between lattice water and the chains, together with close stacking of C_6Cl_2 units from adjacent chains, leads to a very compact 3-dimensional network. The same product can be generated directly from iron(II) ion. Weak ferromagnetic coupling between high spin iron(II) centres with $J = +0.47$ cm^{-1} is observed. Isostructural crystalline materials can be obtained in which Fe^{II} has been replaced by Mn^{II}, Zn^{II} and Cd^{II}, a complete structural refinement being carried out in the latter case. Very weak antiferromagnetic coupling between high spin metal centres is observed in the manganese case ($J = -0.17$ cm^{-1}). The structure of a previously reported iron(III) chloranilate, $[Fe_2(C_6Cl_2O_4)_3(H_2O)_4]\cdot 4H_2O$, has been determined by single crystal X-ray diffraction, revealing a dinuclear structure with one bridging chloranilate, two *cis* water ligands and one chelating, "terminal" chloranilate per iron(III) centre.

There is much current interest in the construction of metal–organic polymers in which metal centres are linked by bridging ligands. One problem associated with many of these networks is their relative fragility, manifested in loss of single crystal character when solvent molecules occupying voids in the structures escape from the matrix. In an effort to obtain more robust frameworks we are attempting to put to use the potent chelate effect in ligands which not only bridge but also bind the metal centres at chelating sites.[1]

The dianion of chloranilic acid (2,5-dichloro-3,6-dihydroxy-cyclohexa-2,5-diene-1,4-dione) is a simple, readily available ligand combining chelating and bridging capabilities (**1**). The delocalised π system associated with its planar geometry could provide interesting and possibly useful electronic communication between appropriate metal centres. Networks incorporating metal centres in mixed oxidation states with appropriate bridging ligands offer the prospect of interesting electrical conductivity and chloranilate-based mixed oxidation state networks have the added potential interest that the ligand as well as the metal can, in principle, exist in different oxidation states.
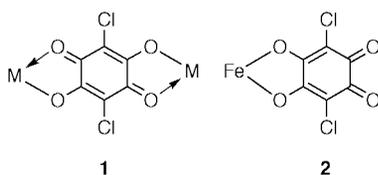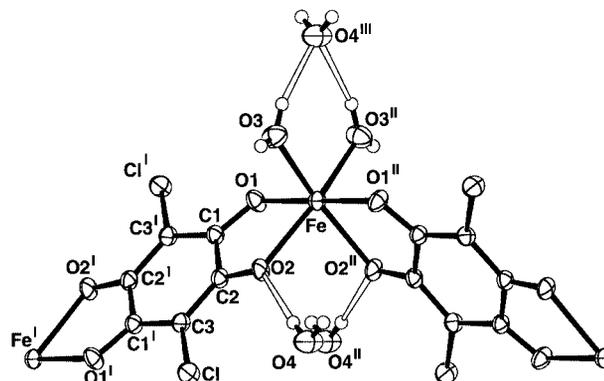
Fig. 1 An ORTEP[2] diagram of $[Fe(can)(H_2O)_2]\cdot H_2O$ showing part of the polymeric chain. Thermal ellipsoids are at the 50% probability level (I $-\frac{1}{2} - x, \frac{1}{2} - y, -z$; II $-x, y, \frac{1}{2} - z$; III $-\frac{1}{2} + x, -\frac{1}{2} + y, z$).

As part of a broad investigation into the co-ordination polymer chemistry of bridging/chelating ligands the results presented here focus on structural and magnetic aspects of some metal chloranilates.

Results and discussion

The reaction between iron(III) perchlorate and chloranilic acid (H$_2$can) in aqueous solution at 85–90 °C yields highly reflective dark crystals of composition $[Fe(can)(H_2O)_2]\cdot H_2O$. A single crystal X-ray diffraction study of this product together with magnetic and Mössbauer data indicate that the iron has been reduced to the iron(II) state. As illustrated in Figs. 1 and 2, chelating chloranilate dianions bridge iron(II) centres to form zigzag chains, all of which are parallel extending in the [101]
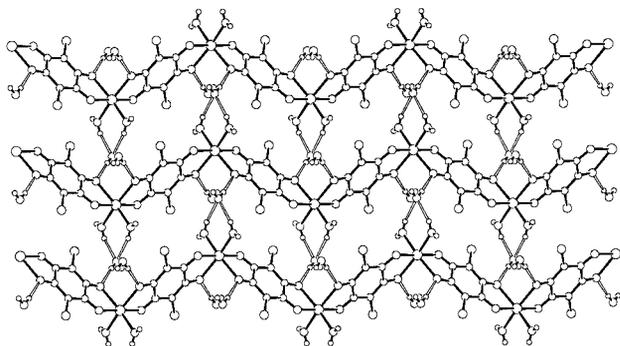
Fig. 2 Representation of three zigzag chains which run parallel to the [1 0 1] direction and some of the hydrogen bonding between them in the [Fe(can)(H$_2$O)$_2$]·H$_2$O structure. Hydrogen bonding which links together chains arranged vertically above and below the ones seen here is omitted for simplicity and is detailed in Fig. 3.
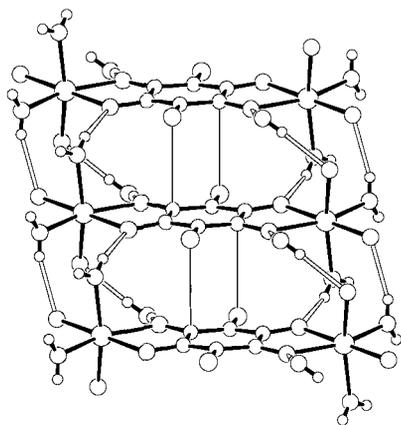
Fig. 3 Stacking in the *a* direction showing the O3···O1 hydrogen bonding that was omitted from Fig. 2 and also the hydrogen bonding of O4 to O3 and O2. "Open" connections represent hydrogen bonds and fine lines represent Cl···C2 contacts of 3.28 Å.

direction. Two *cis* co-ordinated water molecules (O3) complete an octahedral environment around the iron(II) centre. The two co-ordinated water molecules act as hydrogen bond donors to a single unco-ordinated water molecule (O4) in the lattice (O4···O3, 2.755(4) Å). This in turn acts as a hydrogen bond donor to chloranilate oxygen atoms (O2) in two separate adjacent polymeric chains (O4···O2, 2.807(3) Å) as can be clearly seen in Fig. 2. There are two types of chloranilate oxygen atoms, O1 which is *cis* to both co-ordinated water molecules and O2 which is *trans* to one co-ordinated water molecule and *cis* to the other. A third type of hydrogen bond is observed between O1 and the hydrogen atom on the co-ordinated water not involved in hydrogen bonding to the lattice water (O3···O1, 2.891(3) Å). This latter O3···O1 hydrogen bonding brings the C$_6$Cl$_2$ units of adjacent chains into close contact so as to produce stacking in the *a* direction as shown in Fig. 3. The contact of 3.277(3) Å between the Cl atom of one ligand and C2 of a parallel but laterally displaced neighbour is particularly close, significantly less than the sum of the van der Waals radii; indeed this contact would be short even for a carbon–carbon contact. However we note that a similar close C···Cl contact of 3.38 Å is seen in metal-free C$_6$H$_2$Cl$_2$O$_4$·2H$_2$O.[3]

Each zigzag polymeric chain is thus hydrogen bonded to six neighbouring chains (to four others *via* co-ordinated water molecules together with lattice water molecules [O3···O4···O2] and to two others *via* co-ordinated water molecules alone [O3···O1]) to give a compact extended 3-D structure with an average volume per non-hydrogen atom of 15.3 Å^3. This compact packing arrangement gives rise to a small interchain Fe···Fe separation of 4.9199(2) Å which is to
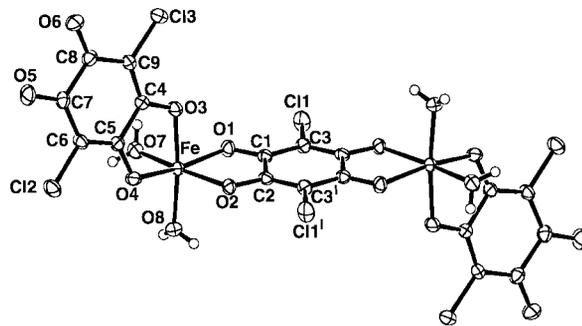
Fig. 4 An ORTEP diagram of [Fe$_2$(can)$_3$(H$_2$O)$_4$]·4H$_2$O. Thermal ellipsoids are at the 50% probability level (I 1 $-x$, $-y$, $-z$).

be compared with the intrachain Fe···Fe separation of 8.092(1) Å.

The Fe–ligand bond distances are all close to 2.1 Å consistent with iron(II) in the high spin electronic configuration indicated by the magnetic and Mössbauer data discussed below (Fe–O1, 2.122(2); Fe–O2, 2.158(2); Fe–O3, 2.094(2) Å).

The formation of the iron(II) product from the iron(III) starting material in the presence of air came as a surprise to us because ligands with negatively charged oxygen donors generally favour Fe^{III} over Fe^{II} to the extent that the reduced forms may be difficult to isolate, requiring careful exclusion of air. It is unclear what caused the reduction of the metal. An identical product can be obtained directly from iron(II) ion by reaction of chloranilic acid with iron(II) sulfate in aqueous solution without any precaution to exclude air.

Magnetic data and Mössbauer spectra of an iron(II) chloranilate compound of reported composition [Fe(can)(H$_2$O)$_2$]$_n$ have been described previously.[4] This product, described as a "dark green precipitate", was obtained from a hot aqueous mixture of iron(II) sulfate and chloranilic acid under a dinitrogen atmosphere. The compound that we isolate, described above, also obtainable from a hot aqueous mixture of iron(II) sulfate and chloranilic acid, but in air, not under dinitrogen, appears to be different. Our compound is obtained in highly crystalline form and the X-ray and the elemental analytical data unquestionably indicate three, not two, molecules of water per iron; in addition, the magnetic and Mössbauer data discussed below are also significantly different. In the earlier study a linear polymeric structure with two *trans* water molecules co-ordinated to the iron(II) centres was proposed but no X-ray crystallographic study was undertaken.

Some other chloranilate derivatives of iron have been reported previously. A material of composition [Fe(can)Cl(H$_2$O)$_3$]·5H$_2$O with chloride bound to the iron was isolated when FeCl$_3$ was used as the source of iron.[5] A single crystal X-ray study of this compound revealed a mononuclear structure with three co-ordinated water molecules in the *mer* configuration and with chelating but not bridging chloranilate. Various bond distances indicated that the "*ortho*-quinone" resonance canonical form of the dianionic ligand represented in the structural diagram **2** was a significant contributor to the overall electronic distribution. Magnetic properties and Mössbauer spectra have been reported for a compound of composition [Fe$_2$(can)$_3$(H$_2$O)$_4$]·4H$_2$O.[4] We have now determined the structure of this compound, shown in Fig. 4, by single crystal X-ray diffraction. It contains discrete centrosymmetric [Fe$_2$(can)$_3$(H$_2$O)$_4$] molecules in which each metal centre carries two *cis* co-ordinated water molecules. Non-bridging, terminal chloranilate, as in the [Fe-(can)Cl(H$_2$O)$_3$]·5H$_2$O example above, and also bridging chloranilate are both present. Differences, although not large, are seen in the C–O bond distances that reflect the significant participation of the *ortho*-quinone resonance contribution **2** in the terminal ligands and the more delocalised electronic arrangement in the bridging ligand (C1–O1, 1.254(4); C2–O2, 1.266(4); C4–O3, 1.287(4); C5–O4, 1.291(4); C7–O5, 1.223(4);

C8–O6, 1.225(4) Å). The Fe–O distances are significantly shorter than those seen in the polymeric iron(II) derivative as is consistent with the high spin iron(III) configuration indicated by the magnetic and Mössbauer spectral data (distances between the iron and various oxygen atoms are - O4 1.978(3), O8 1.980(3), O3 1.995(3), O1 2.020(3), O7 2.024(3), O2 2.055(3) Å). The intramolecular Fe⋯Fe separation is 7.847(3) Å. The lattice water binds the dinuclear complex molecules together in an extensive hydrogen bonding network but the closest intermolecular Fe⋯Fe separation (6.393(2) Å) is much larger than the inter-chain Fe⋯Fe separation seen in the very compact iron(II) polymer described above. Relatively close intermolecular Cl⋯C contacts of two types are present: face-to-face Cl(2)⋯C(7) contacts of 3.382(4) Å and approximately edge-to-face Cl(3)⋯C(2) contacts of 3.337(4) Å.

This example demonstrates that chloranilate already chelated to one iron(III) centre may have an affinity for a second Fe^{III} reduced to such an extent that it may fail to compete with even weak monodentate ligands such as water. An important message to emerge from this with regard to deliberate crystal engineering of co-ordination networks is that chloranilate cannot be relied upon to act as a bridge under all circumstances.

We have investigated reactions analogous to that above between iron(II) sulfate and chloranilic acid with sulfates of some other divalent metals. Crystalline products were obtained for Mn, Co, Ni, Cu, Zn and Cd. In the case of Cd, beautiful highly reflective crystals of composition [Cd(can)(H$_2$O)$_2$]·H$_2$O were obtained which were shown by a single crystal X-ray study, including a complete structural refinement, to be isostructural with the iron(II) analogue.‡ In the cases of Mn and Zn the crystals were too small for collection of a complete set of X-ray diffraction data but were large enough to provide unit cell dimensions which indicated they were isostructural with the iron(II) and cadmium derivatives. The reactions of Co, Ni and Cu yielded microcrystalline materials unsuitable for single crystal X-ray studies. Powder X-ray diffraction (XRD) clearly indicated that the derivatives of Mn, Fe, Zn and Cd were isostructural and that the bulk products were homogeneous with the same structure as those of the single crystals. Powder XRD of the products with Co, Ni and Cu however indicated significantly different structures, the details of which remain to be discovered. The structure of a material of composition Cu(can)·xH$_2$O has been previously described,[6] although the crystals were reported to deteriorate rapidly, allowing only a crude structural solution. The chloranilate ligand was reported to bridge copper(II) centres carrying two *trans* water ligands yielding a straight chain co-ordination polymer in contrast to the zigzag chain with *cis* water ligands that we observe for the derivatives of divalent Mn, Fe, Zn and Cd. The powder X-ray diffraction patterns we observed for our copper(II) derivative were much broader than those of our other divalent metal derivatives which is consistent with the rapid crystal deterioration reported in the earlier study. The elemental analysis of our sample after exposure to the atmosphere for several days was closely consistent with the formulation Cu(can)·H$_2$O which contrasts with the trihydrate formulation of all the other derivatives. It appears therefore that the copper(II) derivative differs from the others in that it is prone to lose water and that this is responsible for the crystal deterioration.

Magnetic and Mössbauer spectral studies

The Mössbauer spectrum of [Fe(can)(H$_2$O)$_2$]·H$_2$O, measured at 77 K, shows an almost symmetrical quadrupole doublet typical of high spin octahedral Fe^{II}, with isomer shift relative to α-Fe of 1.30 mm s^{-1} and quadrupole splitting of 2.97 mm s^{-1}. These

‡ The details of the structure of [Cd(can)(H$_2$O)$_2$]·H$_2$O are so closely similar to those of the iron(II) derivative that we have chosen not to present them here. These details can be obtained from the Supplementary Material.
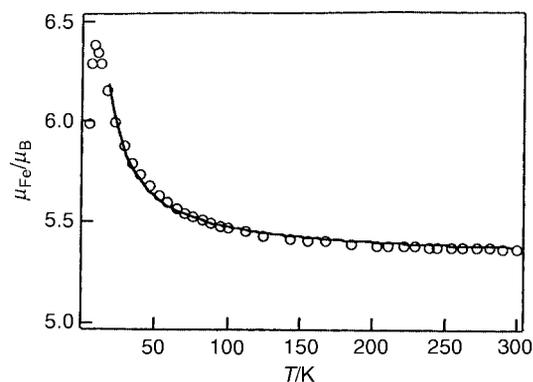
Fig. 5 Plot of μ_{Fe}, per Fe, *versus* temperature for [Fe(can)(H$_2$O)$_2$]·H$_2$O measured in a field of 1 T. The solid line is that calculated using a $S = 2$ chain model and parameters described in the text.
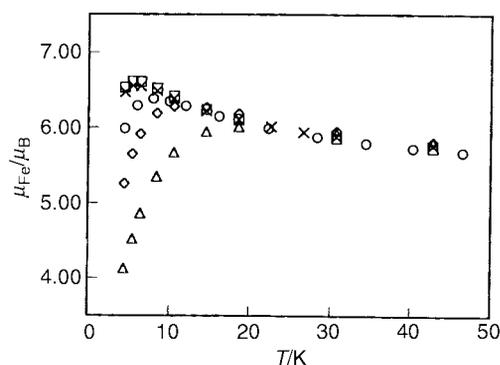
Fig. 6 Plots of μ_{Fe} *versus* temperature for [Fe(can)(H$_2$O)$_2$]·H$_2$O in fields of 0.01 (crosses), 0.1 (squares), 1 (circles), 2 (diamonds), 4 T (triangles).

parameters are significantly higher than those reported,[4] at both 295 and 15 K, for the dihydrate [Fe(can)(H$_2$O)$_2$]$_n$ suggesting that our product differs significantly from the earlier one.

Variable temperature and variable field magnetic susceptibility studies were made on [Fe(can)(H$_2$O)$_2$]·H$_2$O. No long range magnetic order was observed when magnetisation measurements were made in low values of applied field of *ca.* 5 Oe. Interestingly, this polymeric complex of Fe^{II} displays intrachain ferromagnetic coupling. The moments increase gradually with decreasing temperature towards a maximum value (μ_{max}), at about 8 K, when measured in a field of 1 T. Data are given in Fig. 5. Below μ_{max}, the μ_{Fe} values decrease sharply, suggesting a competing interchain antiferromagnetic coupling and/or zero field splitting effects on the high spin iron(II) centres. There is an alternative reason for the μ_{max} behaviour, which we give below. In a field of 1 T the magnetic moment at 300 K is 5.36 μ_B and $\mu_{max} = 6.38$ μ_B. The room temperature value is typical of those anticipated for orbitally degenerate $^5T_{2g}$ states on Fe^{II}, split to some degree by the ligand field generated by the chloranilate and water ligands. The μ_{max} value, per Fe^{II}, is as expected for parallel coupling of the $S = 2$ ions. Use of a Heisenberg linear chain $-2JS_1 \times S_2$ model[7] for $S = 2$ gave a good fit in the temperature range 20 to 300 K for $g = 2.17$ and $J = +0.47$ cm^{-1}. The high effective g value allows for orbital degeneracy on Fe^{II}. The model does not allow the low temperature μ_{max} region to be simulated. There are no other chloranilate bridged iron(II) complexes with which to compare the J value, but it is known that dinuclear chloranilate bridged complexes of Ni^{II} and Cu^{II}[8] are weakly coupled ($J < -12$ cm^{-1}), albeit antiferromagnetically. 2-D and 3-D polymeric copper(II) chloranilate derivatives also show very weak antiferromagnetic coupling.[6,9]

A most interesting effect was observed when the moment was measured in the region of μ_{max} as a function of applied field H. In Fig. 6 we see that, in higher fields of 2 and 4 T, μ_{max} moves to higher temperature and to lower value, the 4.2 K value
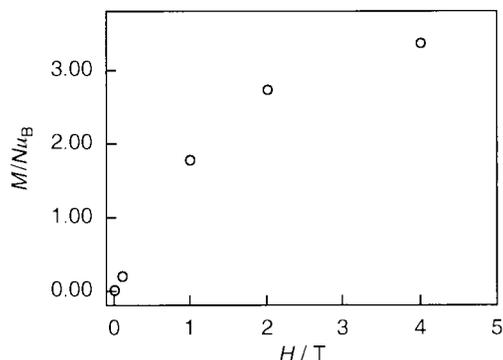
Fig. 7 Magnetisation isotherm for [Fe(can)(H$_2$O)$_2$]·H$_2$O measured at 5 K.

correspondingly decreasing sharply to, for instance, 4.1 μ_B in $H = 4$ T. In a lower field of 0.1 T the μ_{max} moves to lower temperature (*ca.* 6 K) and to a higher value. Then, surprisingly, in $H = 0.01$ T, the maximum remains at 6 K, but the μ_{max} value decreases, as do the μ values at 4.2 K. Thus a plot of μ *vs.* H, at 4.2 K or at the temperature of the maximum, shows a maximum for $H = ca.$ 0.1 T. The corresponding magnetisation isotherm at 5 K, shown in Fig. 7, does not saturate in the highest field used, 4 T, at which the M value of 3.2 $N\mu_B$ is less than that expected (4 $N\mu_B$) probably because of spin–orbit coupling or zero field splitting on Fe^{II}. The μ values are independent of field above 50 K. The field dependent behaviour of Fig. 6 is, we believe, indicative of Zeeman mixing effects rather than interchain antiferromagnetism. We have seen similar effects in μ_{max} *vs.* temperature, albeit not with the maximum in μ_{max} *vs.* H, in spin coupled clusters[10] and in extended polymers such as cobalt(II) tricyanomethanide,[11] which also contains an orbitally degenerate ground state. In essence, it arises because the Zeeman, M_s, levels of lowest energy are very close together and change their energy as the field increases from zero, thus giving rise to differences in thermal population as the temperature is raised from 4.2 K. The precise make up of the lowest levels is complex, since the ferromagnetic coupling as well as spin–orbit coupling and low symmetry ligand field effects will all contribute.

The previously reported material [Fe(can)(H$_2$O)$_2$]$_n$ showed very weak antiferromagnetic coupling with μ(300 K) = 5.8 μ_B and μ(20 K) = 5.5 μ_B.[4] Clearly this product differs significantly from ours.

A search of the literature for polymeric ferromagnetically coupled iron(II) compounds reveals very few examples. Holm and co-workers described dinuclear Schiff base species containing μ-alkoxo bridges with an FeOFe angle of 96° and an Fe···Fe separation of 3.2 Å and $J = +1.2$ cm^{-1}.[12] However, other dinuclear non-heme iron biomodel diiron(II) compounds containing μ-alkoxo and μ-carboxylato bridges showed weak antiferromagnetic coupling.[13] A very early report of the magnetism of Fe^{II}(C$_2$O$_4$)·2H$_2$O also suggests ferromagnetic coupling is present,[14] although discrete dinuclear μ-oxalato iron(II) complexes display antiferromagnetism and zero field splitting effects.[15] Zigzag copper(II) chains of the type we describe above, but containing oxalate rather than chloranilate bridges, have recently been shown to display ferromagnetic coupling and thus the sign of the J value may relate to the precise geometry of the chain structure.[16]

The magnetic data for the dinuclear iron(III) complex, [Fe$_2$(can)$_3$(H$_2$O)$_4$]·4H$_2$O, are typical of those expected for a weakly coupled high spin iron(III) dimer. They were fitted well by a Heisenberg $-2J\boldsymbol{S_1}\cdot\boldsymbol{S_2}$ model using the parameters $g = 2.01$, $J = -0.38$ cm^{-1} (zero field splitting was not included). The J value is a little less than that reported for this compound, -0.95 cm^{-1}.[4] The Mössbauer spectrum of our bulk sample of the dinuclear iron(III) compound at 77 K is essentially in agreement with that reported but also indicates the presence of

7.8% (by area) of the iron(II) polymer with isomer shift and quadrupole splitting values identical to those given above.

The chain polymer [Mn^{II}(can)(H$_2$O)$_2$]·H$_2$O shows very weak antiferromagnetic coupling. The susceptibilities obey a Curie–Weiss law in the range 4.2 to 300 K, with a θ value of -4.5 K. The corresponding μ_{Mn} values decrease very slowly from 5.55 μ_B at 300 K to 5.50 μ_B at 100 K then more rapidly, reaching 3.67 μ_B at 4.2 K. Use of a Fisher chain model for $S = 5/2$, which did not contain zero field splitting terms, gave a J value of -0.17 cm^{-1}.[17]

Experimental

[M(can)(H$_2$O)$_2$]·H$_2$O (M = Mn, Fe, Co, Ni, Zn or Cd) and [Cu(can)(H$_2$O)] from the divalent metal sulfate salts

Chloranilic acid (H$_2$can, 104.5 mg, 0.5 mmol) dissolved in warm water (75 ml) on a steam-bath was combined with a warm solution of MSO$_4$·xH$_2$O (0.500 mmol) (M = Mn, Fe, Co, Ni, Cu, Zn or Cd) in water (25 ml) also on the steam-bath and the resulting solution left to stand at room temperature. A crystalline precipitate began to form upon standing. After the solution had been left to stand for a week the crystals were filtered off, washed with water and dried in air. Yields and analyses: M = Mn, 127 mg, 80%; calc. for Mn(C$_6$Cl$_2$O$_4$)·3H$_2$O C 22.81, H 1.91, Cl 22.44%, found C 22.78, H 1.99, Cl 22.44%; M = Fe, 86 mg, 54%; calc. for Fe(C$_6$Cl$_2$O$_4$)·3H$_2$O C 22.74, H 1.91, Cl 22.38%, found C 22.45, H 2.08, Cl 21.80%; M = Co, 94 mg, 59%; calc. for Co(C$_6$Cl$_2$O$_4$)·3H$_2$O C 22.52, H 1.89, Cl 22.16%, found C 22.72, H 1.82, Cl 21.89%; M = Ni, 103 mg, 63%; calc. for Ni(C$_6$Cl$_2$O$_4$)·3.5H$_2$O C 21.92, H 2.15, Cl 21.57%, found C 21.87, H 2.13, Cl 21.54%; M = Cu, 106 mg, 73%; calc. for Cu(C$_6$Cl$_2$O$_4$)·H$_2$O C 24.98, H 0.70, Cl 24.57%, found C 24.77, H 0.63, Cl 24.41%; M = Zn, 144 mg, 88%; calc. for Zn(C$_6$Cl$_2$O$_4$)·3H$_2$O C 22.08, H 1.85, Cl 21.72%, found C 21.96, H 1.85, Cl 21.42%; M = Cd, 164 mg, 88%; calc. for Cd(C$_6$Cl$_2$O$_4$)·3H$_2$O C 19.30, H 1.62, Cl 18.99, found C 19.61, H 1.64, Cl 18.90%.

[Fe(can)(H$_2$O)$_2$]·H$_2$O from Fe^{III}

A solution of Fe(ClO$_4$)$_3$·9H$_2$O (207 mg) in water (25 ml) was added to a solution of chloranilic acid (136 mg) in water. The resulting solution was divided into two parts: a 25 ml sample which was left to stand at room temperature and a 100 ml sample which was placed on a steam-bath for two days in an enclosed vessel to prevent evaporative loss. The solution at room temperature did not yield any precipitate. The heated solution yielded 16 mg (25%) of well formed dark crystals of [Fe(can)(H$_2$O)$_2$]·H$_2$O. The preparation of [Fe$_2$(can)$_3$(H$_2$O)$_4$]·4H$_2$O has been described previously.[3]

Crystallography

Crystal data of [Fe(C$_6$O$_4$Cl$_2$)(H$_2$O)$_2$]·H$_2$O. C$_6$H$_6$Cl$_2$FeO$_7$, $M = 316.86$, monoclinic, space group $C2/c$ (no. 15), $a = 4.9199(2)$, $b = 14.255(1)$, $c = 14.011(3)$ Å, $\beta = 94.980(7)°$, $U = 94.980(7)$ Å^3, $T = 293$ K, $Z = 4$, μ(Mo-Kα) = 17.632 mm^{-1}, 1230 reflections measured, 1007 unique ($R_{int} = 0.0348$) which were used in all calculations. Final R values: $wR2 = 0.0802$ (all data), $R1 = 0.0315$ [$I > 2\sigma(I)$]. Structure solved using SHELXS 86[18] and refined using SHELXL 97.[19]

Crystal data of [Cd(C$_6$O$_4$Cl$_2$)(H$_2$O)$_2$]·H$_2$O. C$_6$H$_6$CdCl$_2$O$_7$, $M = 373.41$, monoclinic, space group $C2/c$ (no. 15), $a = 4.8655(5)$, $b = 14.575(1)$, $c = 14.252(2)$ Å, $\beta = 92.95(1)°$, $U = 1009.3(2)$ Å^3, $T = 293$ K, $Z = 4$, μ(Mo-Kα) = 22.451 mm^{-1}, 1261 reflections measured, 1043 unique ($R_{int} = 0.0106$) which were used in all calculations. Final: $wR2 = 0.0684$ (all data), $R1 = 0.0243$ [$I > 2\sigma(I)$]. Structure solved and refined as above.

Magnetic and Mössbauer spectral measurements

Details of the magnetic[20] and Mössbauer spectral[21] measurements were as described previously.

Acknowledgements

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