Crystal Structure and Magnetic Properties of the Complex $[Cu(en)_2]_2[\{Fe(edta)\}_2O]\cdot 2H_2O$.† A Heterobimetallic Cu^{II}–Fe^{III} System containing a μ-Oxo-di-iron(III) Moiety

Pedro Gomez-Romero and Geoffrey B. Jameson *
Department of Chemistry, Georgetown University, Washington, D.C. 20057, U.S.A.
Juan J. Borras-Almenar, Emilio Escriva, Eugenio Coronado,* and Daniel Beltran *
Departament de Quimica Inorganica, Universitat de Valencia, Dr. Moliner 50, Burjassot (Valencia), Spain

The synthesis, structure, and magnetic properties are reported for the co-ordination polymer $[Cu(en)_2]_2[\{Fe(edta)\}_2O]\cdot 2H_2O$ (en = ethylenediamine, edta = ethylenediamine-*NNN'N'*-tetra-acetate). Crystals are monoclinic, space group *C2/c*, $a = 16.662(2)$, $b = 15.254(3)$, $c = 18.751(3)$ Å, $\beta = 102.58(1)°$, $Z = 8$ (for empirical formula $C_{14}H_{31}CuFeN_6O_{10}$); $R = 0.0296$ ($R' = 0.0310$) for 316 parameters and 3 105 observed reflections. The complex is a three-dimensional polymer consisting of μ-oxo iron(III) dimers connected with two different $Cu(en)_2$ moieties [Cu(1) and Cu(2)] sitting on non-equivalent inversion centres. The Cu–Fe connections are in one case [Cu(2)] through an iminoacetate group of the edta, and in the other *via* a hydrogen bond that connects Cu(1) with a carboxylate group co-ordinated to Fe. The extended covalently bonded network results in ordered bimetallic chains [$\cdots$ Cu(2) $\cdots$ Fe–Fe $\cdots$ Cu(2) $\cdots$], with Cu(1) hydrogen bonded to them. The monodentate co-ordination of the COO groups bonded to Cu(2) precludes any significant magnetic interaction between Cu and Fe. Thus, magnetic susceptibility data down to 4 K are adequately described by assuming a coupled μ-oxo iron(III) dimer ($J = -85$ cm^{-1}, $H = -2JS_1S_2$) and two Cu^{II} monomers. The possibility of increasing the magnetic dimensionality of this system following a procedure similar to that reported for other edta bimetallic compounds is suggested.

One of the major advances in magnetochemistry in the past few years has been related to the planned synthesis of structurally ordered bimetallic materials of variable magnetic dimensionality.[1,2] In this context, we have shown the usefulness of ethylenediamine-*NNN'N'*-tetra-acetate (edta) and edta-like ligands (such as cyclohexane-1,2-diamine-*NNN'N'*-tetra-acetate, cdta), in order to prepare several series of isostructural bimetallic compounds in which different metal ions can be accommodated at different sites with ease. Thus, by using edta, we can isolate the series $[MM'(edta)]\cdot 6H_2O$ (M = Mn^{II}, Co^{II}, or Ni^{II}; M' = Co^{II}, Ni^{II}, or Cu^{II}) where the structure consists of ordered bimetallic chains,[3–5] and the series $[MM'(edta)]\cdot 2H_2O$ (M, M' = Mg^{II}, Co^{II}, Ni^{II}, or Zn^{II}), featuring ordered bimetallic layers.[6,7] With cdta, heterobimetallic dimers can be obtained by using the same metals indicated above for the edta hexahydrate series.[8] Our interest in these systems has been related to their distinctive magnetic properties. In fact, they provide an ideal structural support to isolate low-dimensional ferrimagnetic systems.[7,9–12]

All compounds reported up to now have contained only divalent ions. In this work we extend the study of these kinds of systems to solids containing trivalent iron. We report the synthesis, structure, and magnetic properties of a 1:1 Cu–Fe bimetallic complex with edta and ethylenediamine (en), formulated as $[Cu(en)_2]_2[\{Fe(edta)\}_2O]\cdot 2H_2O$ (**1**).

Experimental

Synthesis of $[Cu(en)_2]_2[\{Fe(edta)\}_2O]\cdot 2H_2O$.—Solid sodium hydroxide (3 mmol) was added to a stirred aqueous solution of $[Fe(Hedta)(H_2O)]$ (1.5 mmol), previously prepared according to the procedure of Lambert *et al.*[13] The pH of the resulting solution (*ca.* 9.4) was adjusted to 9.0 and then, solid $[Cu(en)_2][NO_3]_2$ (1.5 mmol) was added with stirring to this solution. Addition of dimethylformamide [dmf, *ca.* 100 cm^3 (about the same volume as that of the above solution)] followed by heating at 40 °C resulted in the growth (after 48 h) of single crystals suitable for *X*-ray diffraction studies; these were sealed in glass capillaries from Charles Supper Co.

Crystal Data.—$C_{14}H_{31}CuFeN_6O_{10}$, $M = 562.8$, monoclinic, space group *C2/c*, $a = 16.662(2)$, $b = 15.254(3)$, $c = 18.751(3)$ Å, $\beta = 102.58(1)°$, $U = 4\,651.4$ Å^3 [by least-squares refinement on diffractometer angles for 24 reflections in the range $30 < 2\theta < 32°$ with Mo-K_{α_1} radiation ($\lambda = 0.7093$ Å)], $D_m = 1.61 \pm 0.02$ g cm^{-3}, $Z = 8$, $D_c = 1.607$ g cm^{-3}; red-purple oblique prism *ca.* 0.25 × 0.20 × 0.12 mm, μ(Mo-K_α) = 15.98 cm^{-1}.

Data Collection and Processing.—Precession photographs showed symmetry and systematic absences consistent with space groups *C2/c* and *Cc*. Picker FACS-I diffractometer, $\theta/2\theta$ scan mode, scan width = $(2.0 + 0.692 \tan\theta)°$, scan speed = 2.0° min^{-1}, graphite-monochromated Mo-K_α radiation; 4 313 data $3.0 < 2\theta < 52°$, $\pm h$, $+k$, $+l$, 3 398 with $F_o^2 > 3\sigma F_o^2$. No significant crystal decay. Lorentz and polarization corrections were applied to the data, as well as an empirical absorption correction (transmission factors 84.8—99.7%).

Structure Analysis and Refinement.—The set of programs included in the SDP (Structure Determination Package Version 3.0 by B.A. Frenz and Associates and Enraf-Nonius, service corporation, New York) was used. Patterson methods were initially used to locate the Fe atom, which was 3.4 Å apart from its two-fold axis image; the most intense peaks in the Patterson map could then be explained if there were two Cu ions on non-equivalent inversion centres. One attempt with direct methods

---

† Bis[bis(ethylenediamine)copper(II)] μ-oxo-bis[(ethylenediamine-*NNN'N'*-tetra-acetato)ferrate(III)] dihydrate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. Positional parameters with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cu(1)	0.500	0.000	0.000	N(5)	0.497 0(2)	−0.016 2(2)	−0.106 5(2)
Cu(2)	0.500	−0.500	0.000	N(6)	0.536 0(2)	0.123 3(2)	−0.016 4(2)
Fe	0.391 82(3)	−0.199 49(3)	−0.262 54(2)	C(1)	0.273 7(2)	−0.283 0(2)	−0.390 2(2)
O(1)	0.500	−0.189 1(2)	−0.250	C(2)	0.225 8(2)	−0.276 5(2)	−0.330 6(2)
O(W1)	0.660 5(2)	−0.030 7(2)	0.028 9(2)	C(3)	0.395 9(3)	−0.390 0(3)	0.060 3(3)
O(W2)	0.500	−0.592 5(4)	−0.250	C(4)	0.374 9(3)	−0.367 7(3)	−0.019 3(3)
O(11)	0.619 7(2)	−0.389 4(2)	−0.015 9(1)	C(5)	0.494 5(3)	0.072 4(3)	−0.139 4(2)
O(12)	0.570 0(2)	−0.274 5(2)	0.032 4(1)	C(6)	0.554 6(3)	0.128 9(3)	−0.088 7(3)
O(13)	0.387 2(1)	−0.317 6(2)	−0.212 6(1)	C(11)	0.411 5(2)	−0.259 2(2)	−0.412 5(2)
O(14)	0.398 3(2)	−0.461 9(2)	−0.222 6(2)	C(12)	0.405 2(2)	−0.313 6(2)	−0.482 3(2)
O(21)	0.365 2(1)	−0.097 2(2)	−0.331 4(1)	C(13)	0.388 0(2)	−0.377 8(2)	−0.330 2(2)
O(22)	0.271 2(2)	−0.011 2(2)	−0.397 9(2)	C(14)	0.390 7(2)	−0.387 5(3)	−0.249 1(2)
O(23)	0.367 6(1)	−0.139 9(2)	−0.173 2(1)	C(21)	0.225 9(2)	−0.116 3(2)	−0.322 0(2)
O(24)	0.283 1(2)	−0.132 5(3)	−0.097 6(2)	C(22)	0.291 1(2)	−0.070 9(3)	−0.353 3(2)
N(1)	0.363 9(2)	−0.288 9(2)	−0.358 6(1)	C(23)	0.234 8(2)	−0.204 2(3)	−0.211 2(2)
N(2)	0.253 9(2)	−0.199 3(2)	−0.284 1(1)	C(24)	0.298 5(2)	−0.154 3(3)	−0.156 0(2)
N(3)	0.480 5(2)	−0.419 3(2)	0.078 5(2)	H(W1A)*	0.316(2)	−0.008(3)	−0.051(2)
N(4)	0.399 2(2)	−0.442 5(2)	−0.059 5(2)	H(W1B)*	0.314(3)	−0.029(4)	−0.497(3)

* Atom refined isotropically.

Table 2. Bond distances (Å) and angles (°) for (**1**) with estimated standard deviations in parentheses

Cu(1)–O(W1)	2.652(3)	Fe–N(2)	2.245(2)	N(1)–C(11)	1.487(4)	C(5)–C(6)	1.496(6)
Cu(1)–N(5)	2.003(3)	O(11)–C(12)	1.227(4)	N(1)–C(13)	1.479(4)	C(11)–C(12)	1.533(5)
Cu(1)–N(6)	2.018(3)	O(12)–C(12)	1.255(4)	N(2)–C(2)	1.480(4)	C(13)–C(14)	1.519(5)
Cu(2)–O(11)	2.678(3)	O(13)–C(14)	1.275(4)	N(2)–C(21)	1.477(5)	C(21)–C(22)	1.510(5)
Cu(2)–N(3)	1.999(3)	O(14)–C(14)	1.234(5)	N(2)–C(23)	1.471(5)	C(23)–C(24)	1.515(5)
Cu(2)–N(4)	2.005(3)	O(21)–C(22)	1.277(4)	N(3)–C(3)	1.447(5)	H(W1A)–O(W1)	0.78(4)
Fe–O(1)	1.773 5(5)	O(22)–C(22)	1.232(5)	N(4)–C(4)	1.471(6)	H(W1A)–O(24)	2.11(4)
Fe–O(13)	2.039(2)	O(23)–C(24)	1.280(5)	N(5)–C(5)	1.482(6)	H(W1B)–O(W1)	0.81(6)
Fe–O(21)	2.012(2)	O(24)–C(24)	1.225(5)	N(6)–C(6)	1.458(6)	H(W1B)–O(22)	2.15(6)
Fe–O(23)	2.022(3)	N(1)–C(1)	1.493(4)	C(1)–C(2)	1.511(5)		
Fe–N(1)	2.226(3)			C(3)–C(4)	1.497(7)		
O(W1)–Cu(1)–N(5)	89.3(1)	O(13)–Fe–N(2)	86.8(1)	C(21)–N(2)–C(23)	112.5(3)	O(14)–C(14)–C(13)	118.1(3)
O(W1)–Cu(1)–N(6)	82.9(1)	O(21)–Fe–O(23)	97.3(1)	N(1)–C(1)–C(2)	111.0(2)	N(2)–C(21)–C(22)	113.7(3)
N(5)–Cu(1)–N(6)	84.7(1)	O(21)–Fe–N(1)	88.77(9)	N(2)–C(2)–C(1)	109.8(3)	O(21)–C(22)–O(22)	123.3(4)
O(11)–Cu(2)–N(3)	86.5(1)	O(21)–Fe–N(2)	79.0(1)	N(3)–C(3)–C(4)	108.0(4)	O(21)–C(22)–C(21)	117.2(3)
O(11)–Cu(2)–N(4)	102.5(1)	O(23)–Fe–N(1)	154.3(1)	N(4)–C(4)–C(3)	107.7(3)	O(22)–C(22)–C(21)	119.5(3)
N(3)–Cu(2)–N(4)	83.6(1)	O(23)–Fe–N(2)	76.53(9)	N(5)–C(5)–C(6)	107.8(3)	N(2)–C(23)–C(24)	110.3(3)
O(1)–Fe–O(13)	99.1(1)	N(1)–Fe–N(2)	80.2(1)	N(6)–C(6)–C(5)	108.0(4)	O(23)–C(24)–O(24)	123.6(3)
O(1)–Fe–O(21)	95.2(1)	Fe–O(1)–Fe	169.7(2)	N(1)–C(11)–C(12)	117.9(3)	O(23)–C(24)–C(23)	116.7(3)
O(1)–Fe–O(23)	103.32(9)	C(1)–N(1)–C(11)	110.6(2)	N(1)–C(13)–C(14)	113.3(3)	O(24)–C(24)–C(23)	119.7(4)
O(1)–Fe–N(1)	100.9(1)	C(1)–N(1)–C(13)	111.7(3)	O(11)–C(12)–O(12)	126.3(3)	H(W1A)–O(W1)–H(W1B)	96.(5)
O(1)–Fe–N(2)	174.1(1)	C(11)–N(1)–C(13)	112.4(3)	O(11)–C(12)–C(11)	119.5(3)	O(W1)–H(W1A)–O(24)	164.(3)
O(13)–Fe–O(21)	162.63(9)	C(2)–N(2)–C(21)	111.8(2)	O(12)–C(12)–C(11)	114.1(3)	O(W1)–H(W1B)–O(22)	167.(4)
O(13)–Fe–O(23)	89.0(1)	C(2)–N(2)–C(23)	113.8(3)	O(13)–C(14)–O(14)	124.5(3)		
O(13)–Fe–N(1)	78.92(9)			O(13)–C(14)–C(13)	117.4(3)		

(MULTAN 11/82) failed to show the same heavy-atom co-ordinates calculated from the Patterson map. Successive difference Fourier syntheses and full-matrix refinements revealed the rest of the atoms. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms from the water molecule were found using difference Fourier maps, the rest were fixed at their calculated positions, and were assigned thermal parameters (B) one unit larger than the atoms to which they were bonded. The weighting scheme was of the form $1/w = \sigma_I^2 + (0.03I)^2$. A final difference Fourier synthesis was essentially featureless (max. 0.389 e Å^{-3}). The final data/parameter ratio was 3 105/316; $R = 0.0296$ ($R' = 0.0310$). Final atomic co-ordinates are given in Table 1; bond distances and angles are in Table 2. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

Magnetic Susceptibility.—Magnetic measurements were performed over the temperature range 4—300 K using a pendulum-type apparatus. The susceptibilities were corrected for the diamagnetism of the constituent atoms and for the temperature-independent paramagnetism of the copper ion (estimated to be -660×10^{-6} and 60×10^{-6} cm^3 mol^{-1} per Cu$^{\text{II}}$ ion, respectively). The magnetic susceptibility data were then fit to the equation below, where the first term refers to the susceptibility (per mole of Fe$^{\text{III}}$) of an exchange-coupled $S = \frac{5}{2}$ dimer,[14] and the second one to the susceptibility of a paramagnetic $S = \frac{1}{2}$ ion (per mole of Cu$^{\text{II}}$); $P = 2\,(e^{-x} + 5e^{-3x} + 14e^{-6x} + 30e^{-10x} + 55e^{-15x})$, $Q = 1 + 3e^{-x} + 5e^{-3x} + 7e^{-6x} + 9e^{-10x} + 11e^{-15x}$,

$$\chi = [N\beta^2 g^2(\mathrm{Fe})/kT](P/Q) + [N\beta^2 g^2(\mathrm{Cu})\cdot S(S+1)]/3k(T-\theta)$$

$x = 2J/kT$; J is the antiferromagnetic coupling constant Fe^{III}–Fe^{III} and θ is the Weiss constant of the paramagnetic ion.

Results and Discussion

Synthesis Strategy for the Fe^{III}–edta *System*.—The reactions of iron(III) complexes of edta in aqueous solution have been widely investigated.[15–17] Thus, the identity of the major species as well as the thermodynamics and kinetics governing their interconversion have been established. It has been shown[15,16] that the iron(III) complex of edta, $[Fe(edta)(H_2O)]^-$ is hydrolysed by alkalis to give equilibrium mixtures of monohydroxy monomers, $[Fe(edta)(OH)]^{2-}$, and μ-oxo binuclear complexes, $[\{Fe(edta)\}_2O]^{4-}$. In a subsequent step dihydroxy monomers, $[Fe(edta)(OH)_2]^{3-}$, are formed. By varying the pH we can control the amount of the hydroxy complexes, but not the dimerization reaction of the monohydroxy complex, which is pH independent. Thus, at pH 9 only monohydroxy and dimeric species are present in a ratio that depends on Fe(edta) concentration and temperature. It has been pointed out[17] that in concentrated solutions and at moderately low temperatures, the μ-oxo dimer is the predominant species. Otherwise (*i.e.* dilute solutions and at temperatures above 100 °C) the monohydroxy complex is the predominant species. Furthermore, under these conditions, Fe^{III} oxidizes co-ordinated edta, the monohydroxy species being the reactive intermediate.

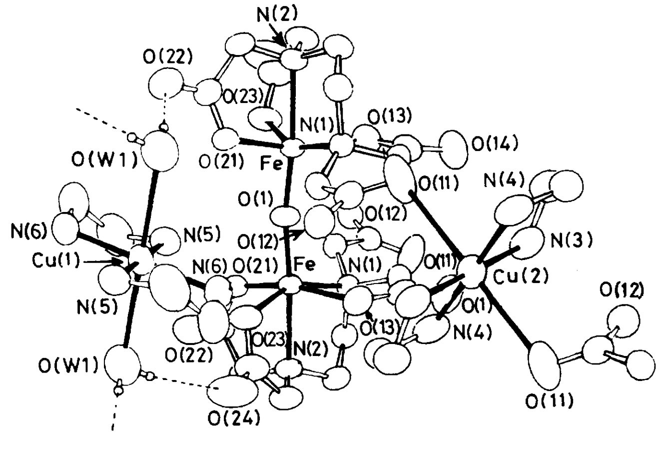


Figure 1. ORTEP diagram showing the co-ordination of the metal ions and their connections through iminoacetate and hydrogen bonds. Cu(1) and Cu(2) occupy non-equivalent inversion centres, while the Fe atoms sit in general positions and are related by a two-fold axis

In view of these facts we have carried out the synthesis at pH 9 and room temperature (r.t.) since under these conditions the stable μ-oxo dimer is the predominant species and no redox reactions are expected to occur.

Description of the Structure of (**1**).—Compound (**1**) is a crystalline three-dimensional polymer consisting of Fe(edta) μ-oxo dimers connected with $Cu(en)_2$ moieties sitting on two non-equivalent inversion centres. In one case the ligand edta provides a carboxylate group that co-ordinates axially to the Cu(2) ion. In the other, a water molecule axially co-ordinated to Cu(1) forms a hydrogen bond with a carboxylate co-ordinated to the Fe atom (Figure 1). The co-ordination geometries of the three crystallographically independent metal centres, as shown in Table 2, are typical of this type of compound, and are in good agreement with other values found in the literature.[18–20]

Notice the close similarity between the geometry of the oxo-bridged Fe^{III}(edta) dimer and that found in the Fe^{III}(hedta) dimer[19] (hedta = *N*-hydroxyethylenediamine-*NN′N′*-triacetate). Thus, we observe the same type of co-ordination geometry around Fe^{III}; the usually hexadentate edta ligand acts here as pentadentate, the sixth arm (an acetate group) being bound to a copper ion. On the other hand, both Fe–O–Fe angles and Fe–O(oxo) distances are very similar [169.7(2)°, 1.773 5(5) Å in the edta system, and 165.0(8)°, 1.79(1) Å for hedta,[19] respectively]. The only noticeable difference is the small increase in the bridging angle that is likely due to steric constraints imposed on the edta by the $[Cu(en)_2]^{2+}$ moiety (in the hedta case the counter ion is $[H_2en]^{2+}$, which does not interact with the dimer).

The connections among metal centres are shown in Figure 2; each Cu(1) cation is connected with four Fe atoms through hydrogen bonds as described previously (two pairs of symmetry related connections), and each Cu(2) obtains its axial carboxylates from two symmetry related Fe(edta) moieties. Some relevant intermetallic distances are: Fe···Fe 3.533(1), Fe···Cu(1) 5.734(1), Fe′···Cu(1) 5.986(1), Fe···Cu(2) 6.681(1) Å.

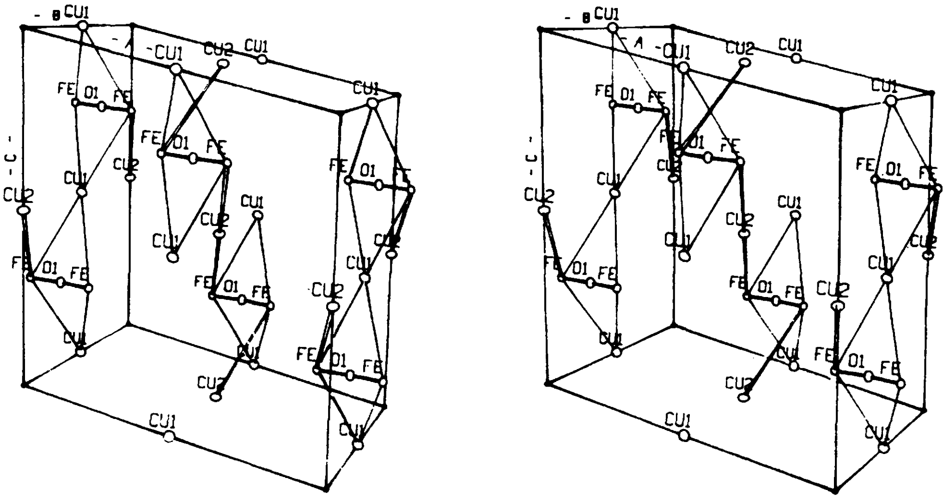
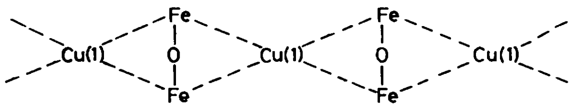


Figure 2. Schematic stereoview of the unit-cell contents emphasizing the connections among metal centres. Bold lines represent strong Fe–O bonds, double lines indicate covalent bridges through iminoacetate groups, and single lines denote hydrogen-bonding connections

As seen in Figure 2 the metallic centres are interconnected forming alternating sheets of Cu and Fe ions parallel to the *bc* plane; within these, pairs of Fe atoms are bridged by the μ-oxo group, which provides most certainly the best pathway for a strong magnetic interaction between them. On the other hand, with regard to the Cu–Fe connections, we can note the following. (*i*) The Cu(2) is linked to an Fe atom through a covalent iminoacetate group ($-N-CH_2-COO-$); this connection is reproduced by symmetry, and an ordered bimetallic chain of the type [$\cdots$Cu(2)$\cdots$Fe–Fe$\cdots$Cu(2)$\cdots$Fe–Fe$\cdots$] is formed. (*ii*) The Cu(1)–Fe link occurs *via* two different hydrogen bonds that connect Cu(1) with the two iron atoms of a dimer through co-ordinated carboxylates; the extended network results in a ladder-like bimetallic chain featuring a sequence of Cu–(Fe–Fe)–Cu ribbons (below).



Both Cu(1) and Cu(2) schemes are not likely to allow any Cu–Fe magnetic interaction since on the one hand, the COO^- group itself is not bridging the two ions but rather co-ordinates to the Cu(2) in a monodentate fashion; on the other hand, although the Fe$\cdots$Cu(1) separations are shorter than Fe$\cdots$Cu(2), the nature of the bridging network is very unfavourable to support any exchange interaction.

Magnetic Susceptibility.—As expected from the presence of magnetically isolated Cu^{II}, the magnetic susceptibility increases continuously on cooling. Much more information can be obtained in this case from the plot of the effective magnetic moment, $\mu_{eff.}$(Fe) (Figure 3). We observe that this decreases gradually as the temperature is lowered, from *ca.* 2.9 (at r.t.) to 2.1 (at 40 K), then stays nearly constant down to 20 K, and finally decreases to 1.9 (at 4 K).

On the basis of the structure this compound can be magnetically viewed as containing an oxo-bridged Fe^{III} binuclear moiety and two Cu^{II} monomers. Then, the observed behaviour can be understood as coming from two independent contributions, namely (*i*) an exchange-coupled $S = \frac{5}{2}$ dimer and (*ii*) two paramagnetic $S = \frac{1}{2}$ ions. Fitting the experimental data to this model (see Experimental section) gave as the best set of parameters: $J = -85$ cm^{-1}, g(Cu) = 2.45, and $\theta = -1.1$ K. In the fit the Lande factor of Fe^{III} has been kept constant and equal to 2.00. The resulting g(Cu) value is undoubtedly too large; this is likely to be an artifact due to the presence of monomeric $S = \frac{5}{2}$ Fe^{III} impurities. Thus, taking g(Cu) = 2.1, this effect can be accounted for if an amount of *ca.* 3% of the total iron is present as monomeric impurity. Since the dimer contribution to the total susceptibility is not dominant, the J value we obtain may be affected by a larger than usual error (*ca.* 5%). This J value falls, within experimental error, at the lower limit of the range found for all other singly bridged symmetrical non-haem μ-oxo di-iron(III) complexes (-90 to -110 cm^{-1}).[18] For example, for the hedta and edta μ-oxo Fe dimers J values of -95 and -99 cm^{-1} were found respectively. This result emphasizes once again the insensitivity of the exchange parameter with respect to Fe–O–Fe bridging angles and topology of the Fe^{III} site (nature and number of non-bridging ligands) for this kind of symmetrical system. The Fe–O(oxo) bond distance,[21] the asymmetry of the dimer,[20] and bridging groups additional to the oxygen have been the only structural features proposed to affect appreciably the J value for non-haem dimers. All factors are irrelevant in our case since the Fe–O distance remains in the usual range (1.75—1.80 Å), and the dimer is a symmetrical one.

Conclusions

When preparing heterobimetallic edta compounds ($M \neq M'$) we take advantage of the fact that, in solution, edta is capable of selectively chelating one metal atom to form the stable dianion $[M'(edta)]^{2-}$. The association of this moiety with a second metallic ion M (hydrated) through bridging carboxylates results in the formation of ordered bimetallic solids. In these systems

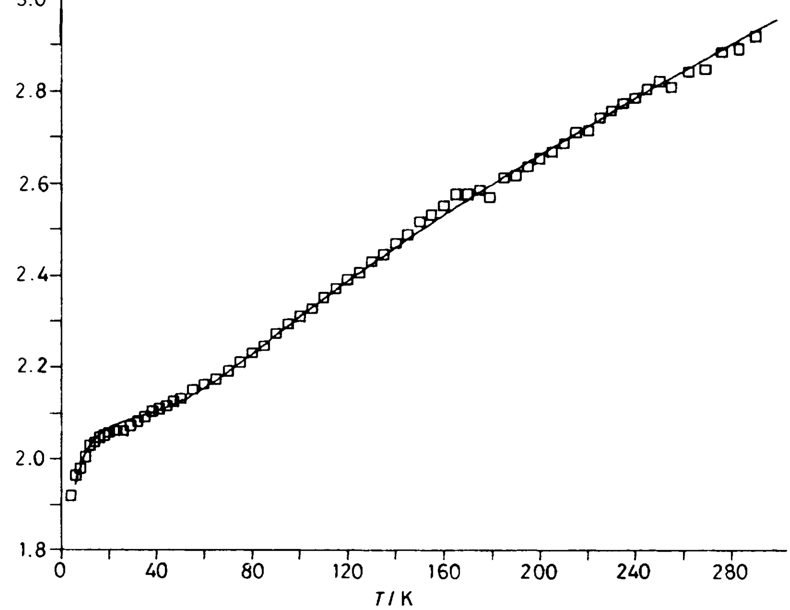


Figure 3. Temperature dependence of the effective magnetic moment for (**1**). The line corresponds to the calculated fit for a μ-oxo iron(III) dimer ($J = -85$ cm^{-1}) plus two isolated Cu ions

edta acts most frequently as hexadentate {for example, in the series of ordered bimetallic chains formulated as $[MM'(edta)]\cdot 6H_2O$}. Nevertheless, by conducting the synthesis under conditions of high temperature and pressure, edta devotes one carboxylate arm to the exclusive co-ordination of the hydrated metal M instead of to the bridging of M and M′ {series $[MM'(edta)]\cdot 2H_2O$}.

In the present work a bimetallic Cu^{II}–Fe^{III} compound with edta has been obtained. Due to the large tendency of Fe^{III} to form μ-oxo dimers, edta co-ordinates to the iron in a pentadentate manner, the loose carboxylate group being co-ordinated to one of the two different copper ions. Unfortunately, the inability of the iminoacetate group to support a Cu–Fe exchange coupling constrains the magnetic interaction pathways to the Fe–Fe moiety.

Previous work done in our laboratory on edta co-ordination polymers has shown that hydrothermal syntheses yield crystalline polymers with less water and more intermetallic COO bridges than the parent compounds prepared under normal conditions.[6] In this sense, the extrusion of some water from the title compound, following a hydrothermal procedure similar to that reported in the edta dihydrate series[6] would open the possibility of preparing new low-dimensional magnetic systems. We consider likely the association of the μ-oxo di-iron(III) moiety with the Cu(1) 'dehydrated' position through a carboxylate bridge, giving rise to an extended magnetic system [. . . Cu–(Fe–Fe)–Cu–(Fe–Fe)– . . .]. Finally, the fact that the solid consists of alternating layers of copper ions and iron dimers makes it a potential precursor for the low-temperature preparation of mixed oxides with controlled metallic order and composition.

Acknowledgements

This work was supported by the Comision Asesora de Investigaciones Cientificas y Tecnicas. G. B. J. acknowledges the support of the National Institute for Diabetes and Digestive and Kidney Diseases through grant no. 5 ROI DK37702-02. We are grateful to the Comite Conjunto Hispano-Norteamericano para la Cooperacion Cultural y Educativa for a fellowship (awarded to P. G-R.). E. C. is grateful for a grant from the Generalitat Valenciana.

References

1 R. Carlin, *Coord. Chem. Rev.*, 1987, **79(3)**, 215.
2 See C. P. Landee, in 'Organic and Inorganic Low Dimensional Crystalline materials,' NATO ASI series B, eds. P. Delhaes and M. Drillon, Plenum, New York, 1987, vol. 168, pp. 75—92.
3 E. Escriva, A. Fuertes, and D. Beltran, *Transition Met. Chem.*, 1984, **9**, 184.
4 D. Beltran, E. Escriva, and M. Drillon, *J. Chem. Soc., Faraday Trans. 2*, 1982, 1773.
5 E. Coronado, M. Drillon, A. Fuertes, D. Beltran, A. Mosset, and J. Galy, *J. Am. Chem. Soc.*, 1986, **108**, 900.
6 P. Gomez-Romero, G. B. Jameson, N. Casan-Pastor, E. Coronado, and D. Beltran, *Inorg. Chem.*, 1986, **25**, 3171.
7 E. Coronado, A. Barba, D. Beltran, R. Burriel, and R. Carlin, pp. 401—404 in ref. 2.
8 A. Fuertes, C. Miravitlles, E. Escriva, and D. Beltran, *Transition Met. Chem.*, 1985, **10**, 432; A. Fuertes, C. Miravitlles, E. Escriva, E. Coronado, and D. Beltran, *J. Chem. Soc., Dalton Trans.*, 1986, 1795; 1987, 1847.
9 M. Drillon, E. Coronado, D. Beltran, and R. Georges, *Chem. Phys.*, 1983, **79**, 449.
10 M. Drillon, E. Coronado, D. Beltran, and R. Georges, *J. Appl. Phys.*, 1985, 3353.
11 M. Drillon, E. Coronado, D. Beltran, J. Curely, R. Georges, P. R. Nugteren, L. J. De Jongh, and J. L. Genicon, *J. Magn. Magn. Mater.*, 1986, **54**, 1507.
12 E. Coronado, P. R. Nugteren, M. Drillon, D. Beltran, L. J. de Jongh, and R. Georges, pp. 405—408 in ref. 2.
13 J. L. Lambert, C. E. Godsey, and L. M. Seitz, *Inorg. Chem.*, 1963, **2**, 127.
14 See W. E. Hatfield, in 'Theory and Applications of Molecular Paramagnetism,' eds. E. A. Boudreaux and L. N. Mulay, Wiley, New York, 1976.
15 G. McLendon, R. J. Motekaitis, and A. Martell, *Inorg. Chem.*, 1976, **15**, 2306 and refs. therein.
16 K. C. Francis, D. Cummins, and J. Oakes, *J. Chem. Soc., Dalton Trans.*, 1985, 493.
17 R. J. Motekaitis, A. E. Martell, D. Hayes, and W. W. Freiner, *Can. J. Chem.*, 1980, **58**, 1999.
18 K. S. Murray, *Coord. Chem. Rev.*, 1974, **12**, 1.
19 S. J. Lippard, H. J. Schugar, and C. Walling, *Inorg. Chem.*, 1967, **6**, 1825; H. J. Schugar, G. R. Rossman, C. G. Barraclough, and H. B. Gray, *J. Am. Chem. Soc.*, 1972, **94**, 2683.
20 See, for example, P. Gomez-Romero, G. C. DeFotis, and G. B. Jameson, *J. Am. Chem. Soc.*, 1986, **108**, 851.
21 D. L. Jameson, C. L. Xie, D. N. Hendrickson, J. A. Potenza, and H. J. Schugar, *J. Am. Chem. Soc.*, 1987, **109**, 740.

Received 15*th January* 1988; *Paper* 8/00180D