# Magnetic and Electrochemical Studies on the Series $[\mathrm{Cr}_n\mathrm{Fe}_{3-n}(\mu_3\text{-O})(\mathrm{gly})_6(\mathrm{H_2O})_3][\mathrm{NO_3}]_7\cdot x\mathrm{H_2O}$ (gly = glycine; $n$ = 0, 1, 2, or 3) and on the Mixed-valence Complex $[\mathrm{Fe^{II}Fe^{III}}_2(\mu_3\text{-O})(\mathrm{gly})_6(\mathrm{H_2O})_3]\mathrm{Cl}_6$

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A series of oxo-centred trinuclear glycinate-bonded complexes $[\mathrm{Cr}_n\mathrm{Fe}_{3-n}(\mu_3\text{-O})(\mathrm{gly})_6(\mathrm{H_2O})_3][\mathrm{NO_3}]_7\cdot x\mathrm{H_2O}$ (gly = glycine; $n$ = 0, 1, 2, or 3) has been synthesised. $[\mathrm{Fe^{II}Fe^{III}}_2(\mu_3\text{-O})(\mathrm{gly})_6(\mathrm{H_2O})_3]\mathrm{Cl}_6$ has also been prepared and this is the first example of a mixed-valence *triangulo* O,O-glycinate bonded complex. Detailed magnetic data for all five complexes down to liquid-nitrogen temperature are discussed and electrochemical data for the complexes are also reported.

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The increasing interest in metal–amino acid systems is attributed to their potentials as models for understanding biologically important molecules. Although amino acids are known to form complexes with metals in either the neutral Zwitterionic form (**1**) or in the anionic form (**2**), the latter type is by far the most common among the published monomeric solid-state structures.[1-3]

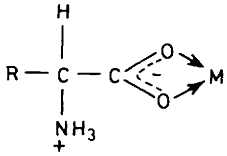
However, dimeric structures where M = $\mathrm{Cu^{II}}$,[4] $\mathrm{Cr^{II}}$,[5] $\mathrm{Rh^{II}}$,[6] $\mathrm{Mo^{II}}$,[7] and $\mathrm{Ag^{I}}$[8] have been established recently and contain O,O-glycinate bonded [Type (**1**)] ligands. In addition, Asplund and co-workers[9-11] and Straughan and co-workers[12,13] have demonstrated that O,O-glycinate bonded ligands are also present in the triangular complexes $[\mathrm{M_3}(\mu_3\text{-O})(\mathrm{gly})_6(\mathrm{H_2O})_3]\mathrm{X}_7\cdot x\mathrm{H_2O}$ (gly = glycine; M = $\mathrm{Fe^{III}}$ or $\mathrm{Cr^{III}}$, X = $\mathrm{ClO_4}$ or $\mathrm{NO_3}$). The oxo-centred $\mathrm{Fe^{III}}_3$ trinuclear complex has been suggested as a valuable model compound for the iron-storage compound ferritin.[11]

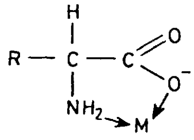
A mixed-metal *triangulo* complex, $[\mathrm{Fe_2Cr}(\mu_3\text{-O})(\mathrm{gly})_6(\mathrm{H_2O})_3][\mathrm{ClO_4}]_7\cdot 6\mathrm{H_2O}$, is also known and its crystal structure shows an ordered arrangement as indicated by thermal parameters;[12] the four symmetry-equivalent cations in each unit cell are arranged such that all of the $\mathrm{Cr}(\mu_3\text{-O})$ bonds are aligned in two directions inclined at only 35.4° to each other. This alignment may imply some kind of magnetic ordering in the crystal.

We have now synthesised for the first time the complete series of oxo-centred trinuclear glycinate-bonded complexes $[\mathrm{Cr}_n\mathrm{Fe}_{3-n}(\mu_3\text{-O})(\mathrm{gly})_6(\mathrm{H_2O})_3][\mathrm{NO_3}]_7\cdot x\mathrm{H_2O}$ ($n$ = 0, 1, 2, or 3). We have also prepared $[\mathrm{Fe^{II}Fe^{III}}_2(\mu_3\text{-O})(\mathrm{gly})_6(\mathrm{H_2O})_3]\mathrm{Cl}_6$ and this is the first example of a mixed-valence *triangulo* O,O-glycinate bonded complex. Elemental analysis and spectroscopic data confirm that all of the compounds in the series are isostructural. We report in detail the magnetic data for all five complexes down to liquid-nitrogen temperature and discuss electrochemical data for the compounds.

## Experimental

All starting materials were used as supplied commercially. Elemental microanalyses were carried out in the Department (Newcastle) and the metal analysis was carried out using a Perkin-Elmer Atomic Absorption 2380 instrument. Infrared spectra were obtained as KBr discs on a Perkin-Elmer 598 spectrometer. Electronic spectra were examined as solids on a Unicam SP1700 while ethanolic solutions were measured on a Perkin-Elmer 550 spectrometer. Electrochemical investigations using a basic potentiostat (250 mA) in conjunction with a chemical electron function generator RB1 were carried out under dry nitrogen gas. Solutions of the oxo-centred trinuclear glycinate-bonded species (0.01 mol dm$^{-3}$ in EtOH) were measured using sodium perchlorate (0.1 mol dm$^{-3}$) as base electrolyte and platinum flags (1 cm$^2$) as working and secondary electrodes. Finally magnetic measurements were made using the Gouy method; details of the particular instrument have been described previously in the literature.[14]


(1)


(2)

*Preparation of the Complexes.*—$[\mathrm{Fe^{III}}_3(\mu_3\text{-O})(\mathrm{gly})_6(\mathrm{H_2O})_3][\mathrm{NO_3}]_7\cdot 3\mathrm{H_2O}$; the literature method was followed using $\mathrm{Fe(NO_3)_3\cdot 9H_2O}$ as the source of iron.[8] The preparations for $[\mathrm{Fe_2Cr}(\mu_3\text{-O})(\mathrm{gly})_6(\mathrm{H_2O})_3][\mathrm{NO_3}]_7\cdot 3\mathrm{H_2O}$, $[\mathrm{FeCr_2}(\mu_3\text{-O})(\mathrm{gly})_6(\mathrm{H_2O})_3][\mathrm{NO_3}]_7\cdot 2\mathrm{H_2O}$ and $[\mathrm{Cr_3}(\mu_3\text{-O})(\mathrm{gly})_6(\mathrm{H_2O})_3][\mathrm{NO_3}]_7\cdot 3\mathrm{H_2O}$ have been described in detail elsewhere.[15]

$[\mathrm{Fe^{II}Fe^{III}}_2(\mu_3\text{-O})(\mathrm{gly})_6(\mathrm{H_2O})_3]\mathrm{Cl}_6$; $\mathrm{FeCl_2\cdot 4H_2O}$ (1 mol) was dissolved in ethanol, and the pH was adjusted to *ca.* 2 using dilute HCl. A concentrated aqueous solution of glycine was added (2 mol) and the reaction mixture was refluxed for 4 h under dry nitrogen at 60 °C. The solution was allowed to cool to room temperature, and the nitrogen flow was ceased. A steady stream of air was then bubbled through the solution until it became dark brown (*ca.* 60 min). The brown solution was allowed to evaporate slowly at room temperature over $\mathrm{P_2O_5}$ in a vacuum desiccator for 2 weeks whereupon air-sensitive black crystals were deposited from the brown mother-liquor. The crystals were filtered off under a stream of dry nitrogen and dried in a vacuum desiccator over $\mathrm{P_2O_5}$. The dried crystals were sealed under nitrogen in glass ampoules to prevent air oxidation of the crystals.

## Results and Discussion

The electronic and diffuse reflectance spectra were used as a guide for characterisation of the species.[15]

Infrared spectra (KBr discs) of the series $[\mathrm{Cr}_n\mathrm{Fe}_{3-n}(\mu_3\text{-O})\text{-}$

$(gly)_6(H_2O)_3][NO_3]_7 \cdot xH_2O$ show the expected bands for ionic nitrate [$\nu_{asym}(NO_3)$ at 1 380 and $\delta(NO_3)$ at 830 cm$^{-1}$] and bridging glycinates [$\nu_{asym}(CO_2)$ at 1 650 and $\nu_{sym}(CO_2)$ at 1 410 cm$^{-1}$]. For $\alpha$-glycine itself the $CO_2$ stretching modes occur at 1 610 [$\nu_{asym}(CO_2)$] and 1 410 cm$^{-1}$ [$\nu_{sym}(CO_2)$]. Thus the separation ($\Delta\nu$) between the symmetric and antisymmetric stretching modes of the carboxylate groups of the co-ordinated glycinate ligand has increased to 240 cm$^{-1}$ and this separation is characteristic for a bridging mode of co-ordination between two metal ions.

*Electrochemical Studies.*—Spencer and Wilkinson[16] have reported electrochemical studies on selected oxo-centred trinuclear species and their results indicate that $[Cr_3(\mu_3\text{-}O)(O_2CMe)_6(H_2O)_3]^+$ exhibits neither reduction nor oxidation waves in the range +2.0 to −1.8 V *vs.* s.c.e. (saturated calomel electrode) while $[Fe_3(\mu_3\text{-}O)(O_2CMe)_6(H_2O)_3]^+$ exhibits an irreversible reduction peak at *ca.* −0.03 V *vs.* s.c.e. When cyclic voltammetry is applied to the series $[Cr_nFe_{3-n}(\mu_3\text{-}O)(gly)_6(H_2O)_3]^{7+}$, it is found that both $[Cr_3(\mu_3\text{-}O)(gly)_6(H_2O)_3]^{7+}$ and $[FeCr_2(\mu_3\text{-}O)(gly)_6(H_2O)_3]^{7+}$ show inactivity in ethanolic solution in the region +2.0 to −2.0 V *vs.* s.c.e. while an irreversible peak is seen at −0.5 V *vs.* s.c.e. for the $[Fe_2Cr(\mu_3\text{-}O)(gly)_6(H_2O)_3]^{7+}$ complex. The most interesting redox properties, however, are produced by an ethanolic solution of the $[Fe_3(\mu_3\text{-}O)(gly)_6(H_2O)_3]^{7+}$ complex when a reversible wave at +0.05 V *vs.* s.c.e. is observed (*cf.* $FeCl_3$ in ethanol gives a reversible redox peak at 0.32 V *vs.* s.c.e.). This difference in potential is significant and it suggests that $[Fe_3(\mu_3\text{-}O)(gly)_6(H_2O)_3]^{7+}$ is unlikely to break down in solution into simple solvated $Fe^{3+}$ ions. A total voltage separation of 78 mV for the tri-iron complex in the cyclic voltammetry experiment suggests that the trinuclear structure stays together in solution and that the electrochemical experiment can be explained in terms of the simple equilibrium (1). An attempt was made to

$$[Fe^{III}{}_3(\mu_3\text{-}O)(gly)_6(H_2O)_3]^{7+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [Fe^{II}Fe^{III}{}_2(\mu_3\text{-}O)(gly)_6(H_2O)_3]^{6+} \quad (1)$$

prepare a small amount of the possible mixed-valence complex

**Table.** Agreement between observed and calculated average atomic susceptibilities

(*a*) $[Fe_3(\mu_3\text{-}O)(gly)_6(H_2O)_3][NO_3]_7 \cdot 3H_2O$

Diamagnetic correction $-264 \times 10^{-6}$ cm$^3$ mol$^{-1}$, $g = 2$, t.i.p. = 0

| | | $10^6[\chi_A(obs.) - \chi_A(calc.)]$/cm$^3$ mol$^{-1}$ | |
|---|---|---|---|
| $T$/K | $10^6\chi_A(obs.)$/ cm$^3$ mol$^{-1}$ | $\alpha = 0.70$, $J = 33.3$ cm$^{-1}$ | $\alpha = 1.57$, $J = 26.3$ cm$^{-1}$ |
| 299.2 | 4 481 | −57 | −8 |
| 269.9 | 4 658 | −45 | −11 |
| 240.3 | 4 879 | −20 | −6 |
| 205.6 | 5 207 | 27 | 10 |
| 171.5 | 5 611 | 68 | 18 |
| 141.8 | 6 037 | 56 | 14 |
| 118.4 | 6 505 | 44 | −17 |
| 84.3 | 7 498 | −54 | 14 |

(*b*) $[Fe_2Cr(\mu_3\text{-}O)(gly)_6(H_2O)_3][NO_3]_7 \cdot 3H_2O$

Diamagnetic correction $-264 \times 10^{-6}$ cm$^3$ mol$^{-1}$, $g = 1.99$, t.i.p. = $40 \times 10^{-6}$ cm$^3$ mol$^{-1}$

| | | $\alpha = 0.73$, $J = 42.4$ cm$^{-1}$ | $\alpha = 1.22$, $J = 26.7$ cm$^{-1}$ |
|---|---|---|---|
| 299.3 | 3 919 | 42 | −41 |
| 269.9 | 4 028 | 25 | −23 |
| 239.9 | 4 151 | 8 | 0 |
| 210.6 | 4 276 | −14 | 18 |
| 181.1 | 4 415 | −35 | 33 |
| 150.9 | 4 589 | −35 | 52 |
| 128.1 | 4 734 | −25 | 47 |
| 108.7 | 4 780 | −95 | −66 |
| 82.6 | 5 142 | 104 | 18 |

(*c*) $[FeCr_2(\mu_3\text{-}O)(gly)_6(H_2O)_3][NO_3]_7 \cdot 2H_2O$

Diamagnetic correction $-251 \times 10^{-6}$ cm$^3$ mol$^{-1}$, $g = 1.97$, t.i.p. = $80 \times 10^{-6}$ cm$^3$ mol$^{-1}$

| $T$/K | $10^6\chi_A(obs.)$/ cm$^3$ mol$^{-1}$ | $10^6[\chi_A(obs.) - \chi_A(calc.)]$/cm$^3$ mol$^{-1}$ $\alpha = 0.995$, $J = 30.3$ cm$^{-1}$ |
|---|---|---|
| 304.2 | 3 581 | 39 |
| 270.1 | 3 674 | 24 |
| 255.7 | 3 729 | 31 |
| 240.4 | 3 768 | 17 |
| 210.5 | 3 863 | 5 |
| 195.1 | 3 934 | 17 |
| 181.1 | 3 954 | −19 |
| 151.7 | 4 047 | −48 |
| 136.4 | 1 445 | −15 |
| 127.3 | 4 139 | −59 |
| 102.8 | 4 229 | −43 |
| 81.9 | 4 458 | 112 |

(*d*) $[Cr_3(\mu_3\text{-}O)(gly)_6(H_2O)_3][NO_3]_7 \cdot 3H_2O$

Diamagnetic correction $-264 \times 10^{-6}$ cm$^3$ mol$^{-1}$, $g = 1.96$, t.i.p. = $116 \times 10^{-6}$ cm$^3$ mol$^{-1}$

| | | $\alpha = 1$, $J = 10.7$ cm$^{-1}$ |
|---|---|---|
| 299.3 | 4 648 | −22 |
| 270.0 | 5 002 | −134 |
| 240.3 | 5 446 | −22 |
| 210.4 | 5 986 | −93 |
| 180.5 | 6 592 | −95 |
| 151.3 | 7 335 | −64 |
| 126.5 | 8 106 | −15 |
| 102.4 | 9 041 | 87 |
| 82.6 | 9 942 | 173 |

(*e*) $[Fe^{II}Fe^{III}{}_2(\mu_3\text{-}O)(gly)_6(H_2O)_3]Cl_6$

Diamagnetic correction $-233 \times 10^{-6}$ cm$^3$ mol$^{-1}$, $g = 2.0$, t.i.p. = $30 \times 10^{-6}$ cm$^3$ mol$^{-1}$

| $T$/K | $10^6\chi_A(obs.)$/ cm$^3$ mol$^{-1}$ | $10^6[\chi_A(obs.) - \chi_A(calc.)]$/cm$^3$ mol$^{-1}$ $J$(binuclear) = 32.8 cm$^{-1}$ |
|---|---|---|
| 299.5 | 6 700 | 46 |
| 269.9 | 7 063 | 37 |
| 240.2 | 7 475 | −1 |
| 210.6 | 8 022 | −17 |
| 180.8 | 8 764 | −18 |
| 151.1 | 9 792 | −16 |
| 126.4 | 11 011 | −15 |
| 102.4 | 12 792 | 22 |
| 83.0 | 14 884 | −30 |

by holding a solution of $[Fe_3(\mu_3\text{-}O)(gly)_6(H_2O)_3]^{7+}$ at its reduction potential for 48 h. Unfortunately, slow evaporation of the resulting solution under $N_2$ produced only crystals of the $[Fe_3(\mu_3\text{-}O)(gly)_6(H_2O)_3]^{7+}$ complex. However, a successful preparation of the mixed-valence $[Fe^{II}Fe^{III}{}_2(\mu_3\text{-}O)(gly)_6(H_2O)_3]^{6+}$ complex was achieved using the method described in the Experimental section. The lack of success using the electrochemical method is possibly due to the extreme ease of oxidation of the reduced complex especially in solution.

*Magnetic Studies.*—Interest in the magnetic properties of the oxo-centred binuclear complexes has centred on the nature of the metal–metal interactions within the $M_3O$ nucleus. Previous interpretations have described the antiferromagnetic interactions in terms of the exchange Hamiltonian (2), where $J$ is the

$$\mathcal{H}_{ij} = -2J_{ij}\Sigma S_i S_j \qquad (2)$$

exchange integral and $S$ is the overlapping integral. In an early paper, Kambe[17] was able to fit the experimental data satisfactorily by assuming that the metal ions were at the apices of an equilateral triangle (*i.e.* $J_{12} = J_{23} = J_{13}$). Several workers have used magnetic measurements as supporting evidence for an oxo-centred trinuclear structure[18,19] and *X*-ray structures, which later became available, confirmed this proposal in the case of a number of trinuclear complexes.[20] More recent work on magnetic properties[21] has suggested that, in many cases, better fits for the susceptibility data can be obtained if it is assumed that the metal ions form an isosceles triangle. In such cases, $J_{12} = J_{23} = \alpha J_{13}$ where $\alpha$ is the ratio of the two exchange integrals. This lowering of symmetry within the $M_3O$ unit has been noted not only in thermomagnetic data,[22] but also in specific heat measurements over a wide range of temperatures.[23]

To retain generality we derived the theoretical expression for the susceptibility of each type of species, on the assumption of an isosceles triangle of atoms, and fitted this to the observed data. Except for the case of the $Cr_3$ species, we have simultaneously adjusted both $J$ and $\alpha$ so as to obtain the best fit between the observed and calculated values of the average atomic susceptibility, $\chi_A$, using the root mean square of the difference as the criterion. In each case the $g$ factor and the temperature-independent paramagnetism (t.i.p.) were assigned on the basis of what appear to be the reasonable values of 1.96 and $116 \times 10^{-6}$ cm$^3$ mol$^{-1}$ respectively for $Cr^{III}$ and 2.00 and 0 respectively for $Fe^{III}$. The final values of the parameters obtained in this way, and the differences between observed and calculated susceptibilities are shown in the Table.

We find that for the $Cr_3$ species the quality of the fit is very insensitive to $\alpha$ which has therefore been taken as unity in the Table.[24] For the $FeCr_2$ species, agreement is much more sensitive to $\alpha$ but a satisfactory fit is only obtainable if its value is very close to 1, indicating that the $M_3O$ unit may be described as essentially an equilateral triangle. By contrast, the $Fe_3$ species gives a very poor fit with $\alpha = 1$ but good fits with $\alpha = 0.7$ and 1.57. This result is in contrast to that for the analogous complex $[Fe_3(\mu_3\text{-}O)(O_2CMe)_6(H_2O)_3]^+$, where the magnetic data can be satisfactorily interpreted in terms of an equilateral triangle of the three iron atoms,[18] and apparently indicate an isosceles triangle of atoms. However, the possible involvement of higher order spin terms or of inter-trimer as well as intra-trimer interaction is not discounted.[25,26] The $Fe_2Cr$ species also gave separate fits, this time at $\alpha = 0.73$ and 1.22 but, in this case, agreement is less sensitive to $\alpha$ and is not markedly worse with $\alpha = 1$.

Another interesting result is shown by the magnetic behaviour of the $[Fe^{II}Fe^{III}{}_2(\mu_3\text{-}O)(gly)_6(H_2O)]Cl_6$ complex. The experimental susceptibilities agree extremely well with values calculated (Table) when the $Fe^{II}Fe^{III}{}_2O$ unit is regarded as binuclear $Fe^{III}{}_2$ unit with negligible interaction from the $Fe^{II}$ ion. This is an extreme case of the weak $Fe^{III}$–$M^{II}$ interaction and strong $Fe^{III}$–$Fe^{III}$ interaction found by Blake *et al.*[27] in the heteronuclear, mixed-valence, trinuclear complexes $[M^{II}Fe^{III}{}_2(\mu_3\text{-}O)(O_2CMe)_6(H_2O)]$ (where M = Ni, Mg, or Mn) for which *X*-ray diffraction results nevertheless indicated equilateral $Fe_2MO$ units. It is however in sharp contrast with the results of Dziobkowski *et al.*[28] for $[Fe^{II}Fe^{III}{}_2(\mu_3\text{-}O)(O_2CMe)_6L_3]$ (L = $H_2O$ or pyridine), who found the $Fe^{III}$–$Fe^{II}$ interaction to be much stronger than the $Fe^{III}$–$Fe^{III}$ interaction. The possibility of our glycinate-bonded complex being a localised class I complex has not been excluded.

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