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Preparations and Structures of some Tris(aquo)-hexa-μ-glycinato-μ_3-oxo Complexes, $[Cr_nFe_{3-n}(\mu_3\text{-}O)(glycine)_6(H_2O)_3](NO_3)_7 \cdot xH_2O$

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Abstract

Three new tris(aquo)-hexa-μ-glycinato-(μ_3-O) complexes with the general formula $[Cr_nFe_{3-n}(\mu_3\text{-}O)(glycinate)_6(H_2O)_3]X_7 \cdot xH_2O$ where n = 3, 2 or 1 have been prepared. The complexes have been characterised by analytical data, i.r. and electronic spectra and the $[Fe_2Cr\text{-}(\mu_3\text{-}O)(glycinate)_6(H_2O)_3](ClO_4)_7 \cdot 6H_2O$ salt has been fully characterised by an X-ray single crystal study. The data for all three complexes are consistent with a planar triangular arrangement of metal atoms, a central μ_3-O atom and six glycinate ligands which bridge across the metal centres using both oxygen atoms of the carboxylate groups *i.e.* retaining a zwitterion configuration. ν_a M_3O and ν_aM–O′ modes have been assigned to the 550–650 and 360–460 cm^{-1} regions of the i.r. spectrum respectively and the electronic spectra of the three glycinates show absorptions which are typical of $M_3(\mu_3\text{-}O)$ planar bridged skeletons.

Introduction

There are many examples reported in the literature of trinuclear (μ_3-oxo)-bridged complexes which involve a wide range of hexa-μ-carboxylate and substituted carboxylate ligands (*e.g.* methanoate, ethanoate, trifluoroethanoate *etc.*) [1]. The reported complexes include mixed-metal (*e.g.* Fe_2Cr and FeCrMg *etc.*) [2, 3] as well as mixed-valence species ($M^{II}M_2{}^{III}$ where M = Fe, Cr, Ru or Mn) [4–7] and these complexes are of considerable current interest because they provide a rich field for studying the electronic communications between different transition metals.

We are interested in isostructural complexes which contain amino-acids as bridging ligands. At low pH values (2–4), the amino acids can be made to co-ordinate to the metal ions via both oxygen atoms of the carboxylate group (because the amino-acid reacts in its zwitterion form) rather than through the more usual N/O mode of co-ordination. Only a few examples of O/O bonded amino-acid complexes have been fully characterised to date, and the $Fe_3(\mu_3\text{-}O)$-amino-acid systems reported by Asplund and co-workers [8] are the only trinuclear complexes of amino-acids to be published so far. For $[Fe_3(\mu_3\text{-}O)(amino\text{-}acid)_6(H_2O)_3]^{7+}$ salts, the trinuclear structure is retained and the complexes are of direct biological relevance.

We have prepared some new analogous complexes which contain CrIII ions, partly to see if this type of O/O amino-acid bridging is widespread outside the Fe(III)–amino-acid system, and also to undertake a systematic study of both the physical and chemical characteristics of these complexes. We report here the preparations, analyses and spectroscopic data for the 4 complexes which make up the series $[Cr_nFe_{3-n}(\mu_3\text{-}O)(glycine)_6(H_2O)_3](NO_3)_7 \cdot xH_2O$ where n = 0, 1, 2 or 3.

Experimental

Method of Preparation

Preliminary attempts to prepare mixed trinuclear Fe(III)/Cr(III)-(μ_3-O)-glycine complexes using the published method [8] given for $[Fe_3(\mu_3\text{-}O)(glycine)_6(H_2O)](ClO_4)_7$ but employing 2:1 or 1:2 mol ratios of $Fe(NO_3)_3 \cdot 9H_2O$ and $Cr(NO_3)_3 \cdot 9H_2O$ respectively were unsuccessful. It appears that, in aqueous solutions, the rate of formation of the $Fe_3\text{-}(\mu_3\text{-}O)$ skeleton is much faster than the rate of formation of the mixed-metal Fe/Cr-(μ_3-O) skeletons and CrIII was not incorporated into the resulting trinuclear complex (see Discussion). The following method does, however, produce the desired mixed-metal complexes containing chromium.

$[Cr_nFe_{3-n}(\mu_3\text{-}O)(glycine)_6(H_2O)_3](NO_3)_7 \cdot xH_2O$ where n = 1 or 2

The appropriate mol ratios (either 2:1 or 1:2) of $Cr(NO_3)_3 \cdot 9H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ respectively were dissolved in the minimum amount of absolute ethanol and glycine (6 mol) was dissolved separately

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in the minimum volume of water. The solutions were mixed together, the pH was adjusted to 2 using dilute HNO_3, and the resulting mixture was refluxed for 2 hr at 60 °C. The solution was cooled to room temperature and allowed to evaporate slowly over a period of 2–3 weeks when crystalline products precipitated out from the concentrated mother solution. The crystals were washed with ethanol and dried over P_2O_5 in a vacuum desiccator.

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

A crystalline sample of the trinuclear chromium salt was prepared by the same method using $Cr(NO_3)_3 \cdot 9H_2O$ (3 mol).

$[Fe_3(\mu_3\text{-}O)(glycine)_6(H_2O)_3](NO_3)_7 \cdot 6H_2O$

This was prepared according to the literature method [9] using $Fe(NO_3)_3 \cdot 9H_2O$ (3 mol).

70% yields were obtained for all 4 trinuclear salts based on the weights of the metal salts used.

Crystalline perchlorate and chloride salts for all 4 complexes have been prepared also from the correct mol ratios of the appropriate metal salts.

Elemental Analyses

Analytical data for the trinuclear nitrate complexes are given in Table I. The relatively poor agreement between the percentage weights found for Fe and Cr and the theoretical values for the mixed-metal complexes is due to mutual interference by the two metals, in both the atomic absorption measurements and in the volumetric methods used. Similar difficulties were encountered with the isostructural trinuclear acetate complexes [10].

Instrumental Details

Infrared spectra were examined as KBr discs on a PE Model 598 spectrometer. Electronic spectra of the complexes were obtained as solids on a Unicam SP1700; ethanolic solutions were examined on a PE Model 550. Raman spectra of α-glycine were recorded using a modified Cary Model 81 instrument. The spectra were excited using the green line (514.5 nm) of a Coherent Radiation Model CR3 argon-ion laser. The spectra were calibrated by reference to the positions of well documented solvent bands and the total uncertainty is ± 2 cm^{-1}.

Results and Discussion

We have confirmed the presence of a trinuclear structure for $[Fe_2Cr(\mu_3\text{-}O)(glycine)_6(H_2O)_3](ClO_4)_7 \cdot 6H_2O$ using X-ray crystallography (see Fig. 1). The details of this structure have been reported elsewhere [11] but the $Fe_2Cr\text{-}(\mu_3\text{-}O)$ planar arrangement is ordered in the crystal and all of the $Cr\text{-}(\mu_3\text{-}O)$ bonds are aligned in two directions inclined at only 35.4°

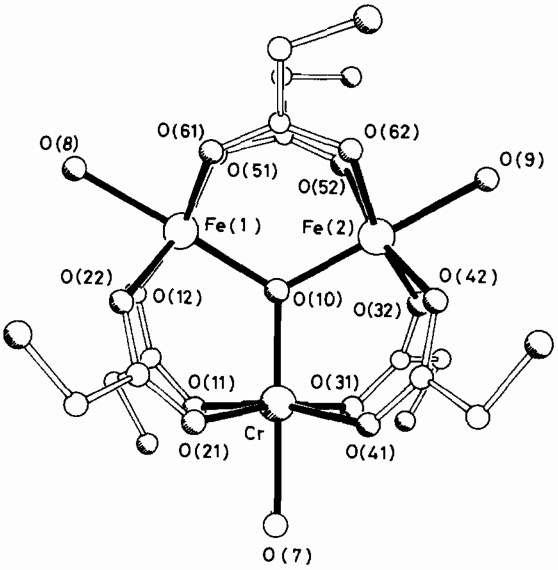

Fig. 1. Structure of $[Fe_2Cr(\mu_3\text{-}O)(glycine)_6(H_2O)_3]^{7+}$ cation.

TABLE I. Elemental Analyses of Cr(III) and Fe(III) (μ_3-O) Trinuclear Complexes.[a]

Glycine complex	Colour		%C	%H	%N	%Fe	%Cr
$[Fe_3(\mu_3\text{-}O)(glycine)_6(H_2O)_3](NO_3)_7 \cdot 6H_2O$	red-brown	Found	11.64	4.01	14.68	13.51	–
		Calc.	11.70	3.90	14.79	13.66	–
$[Fe_2Cr(\mu_3\text{-}O)(glycine)_6(H_2O)_3](NO_3)_7 \cdot 3H_2O$	dark-brown	Found	12.56	3.35	15.55	9.10	4.02
		Calc.	12.52	3.48	15.83	9.56	4.42
$[FeCr_2(\mu_3\text{-}O)(glycine)_6(H_2O)_3](NO_3)_7 \cdot 2H_2O$	dark purple	Found	12.18	3.32	15.24	4.20	8.82
		Calc.	12.29	3.58	15.53	4.86	9.04
$[Cr_3(\mu_3\text{-}O)(glycine)_6(H_2O)_3](NO_3)_7 \cdot 3H_2O$	green	Found	12.39	3.28	15.62	–	13.22
		Calc.	12.37	3.61	15.64	–	13.40

[a] These analyses values are based on the nitrate as counter-ion; satisfactory values have also been obtained for the corresponding perchlorate and chloride salts.

to each other. The ClO_4^- anions are extensively hydrogen-bonded to the protons of the glycine-NH_3^+ groups.

Infrared Spectra

The i.r. spectra of this series of complexes are all very similar over the range 4000–200 cm^{-1} and most of the bands can be readily assigned by comparison with the fundamental vibration frequencies and assignments for α-glycine [12].

The carboxylate stretching frequencies for free α-glycine occur at 1610 cm^{-1} ($\nu_{as}CO_2^-$) and 1410 cm^{-1} ($\nu_s CO_2^-$). For all 4 complexes examined in this paper the $\nu_a CO_2^-$ is raised to 1650 cm^{-1} but $\nu_s CO_2^-$ remains at 1410 cm^{-1}. Thus the separation between the symmetric and antisymmetric stretching modes of the carboxylate groups of co-ordinated glycine ligands is of the order of 200 cm^{-1}, and the separation is characteristic of a bridging mode of co-ordination between two metal ions [13]. The CO_2 modes give rise to slightly narrower bands for the glycinate systems compared with the corresponding carboxylate complexes and we have been able to measure the band positions to within 5 cm^{-1}.

Two regions of particular interest for trinuclear complexes lie between 550–650 and 360–460 cm^{-1}. Both Asplund and co-workers [14] and Cannon and co-workers [15] have assigned new bands in these particular regions to metal–oxygen stretching frequencies. In particular, Cannon has reported that, for trinuclear carboxylate complexes, $\nu_a(M_3O)$ modes occur in the higher of the two ranges while ν_a M–O′ modes (where O′ denotes a carboxylate oxygen present in co-ordinated formate or acetate ligands) are observed at *ca.* 400 cm^{-1}. We have examined the i.r. spectra of our solid glycinate complexes in both of these ranges. However, we must first of all comment on the low frequency (<650 cm^{-1}) vibrational spectrum of solid α-glycine itself.

α-glycine is expected to show 6 fundamental modes below 650 cm^{-1} and 4 of these have been observed and assigned previously [12] [694 (CO_2^- wag), 607 (CO_2^- sym bend), 516 (NH_3^+ torsion) and 504 cm^{-1} (CO_2^- rock)]. The two remaining fundamentals (CCN bend and C–C torsion) have been assigned to *weak* bands at 415 and 325 cm^{-1} respectively in the Raman spectrum of an aqueous solution of glycine [12]. We observe 2 medium-strong bands in the solid state i.r. spectrum at 360 and 210 br cm^{-1} and these bands are also present in the Raman spectrum of solid α-glycine. We have re-examined the Raman spectrum of an aqueous solution of α-glycine in the low frequency region between 450 and 250 cm^{-1} and can discern only a very weak broad band at *ca.* 310 cm^{-1} but no feature at 415 cm^{-1}. The spectra of α-glycine are clearly phase-dependent in this low region, but the correct assignment of the bands does not effect the interpretation of the new bands which are observed below 650 cm^{-1} in the solid state spectra of the trinuclear metal-glycinates.

In addition to the low frequency modes of α-glycine, we observe new features in the spectra of the trinuclear glycinates centred around the δ_{sym} CO_2^- band (which lies at 610 cm^{-1} for these complexes). For the $Cr_3\text{-}(\mu_3\text{-}O)$ complex, a new band of medium intensity is present at 630 cm^{-1} while a different new band of medium intensity is seen at 570 cm^{-1} for the $Fe_3(\mu_3\text{-}O)$ complex. The mixed-metal glycinates $Cr_nFe_{3-n}\text{-}(\mu_3\text{-}O)$ give an intermediate pattern with bands on both sides of the 610 cm^{-1} δ_{sym} CO_2^- band. For $Cr_2Fe\text{-}(\mu_3\text{-}O)$, the feature at 630 cm^{-1} is the more intense of the new pair while the absorption at 570 cm^{-1} is more prominent for the $CrFe_2\text{-}(\mu_3\text{-}O)$ complex. We assign the new bands to the respective $\nu_a(M_3O)$ vibrations.

A similar interpretation can be used for the new broad bands which appears at 450 cm^{-1} (for Cr containing complexes) and 400 cm^{-1} (for Fe containing complexes) and again we follow Cannon's assignment for analogous carboxylate systems and assign the bands to ν_a(M–O′). Both the M–O′ and M_3O glycinate stretching frequencies are slightly lower in position than the corresponding M–O′ and M_3O carboxylate frequencies; the small shift may be ascribed to the extensive intermolecular $\text{-}NH_3^+ \cdots X^-$ hydrogen-bonding which is present in the glycinate systems.

We were unable to observe any other bands in the spectra of the glycine complexes which might be assigned to $\nu_s(M_3O)$ or ν_s(M–O′).

Electronic Spectroscopy

The visible spectra of these complexes are identical to those of the trinuclear μ_3-oxo-bridged carboxylate analogues.

In the case of the $Fe_3(\mu_3\text{-}O)$-glycine complex, the solution spectrum is poorly resolved because the charge-transfer absorption extends into the visible region and it obscures the expected ligand field bands. The solid-state reflectance spectrum of the $Fe_3\text{-}(\mu_3\text{-}O)$-glycinate complex is marginally clearer, with the weak band, assigned by Puri and co-workers [16] to the transition $^6A_1 \rightarrow {}^4T_2$, just observable at 617 nm.

Both the solution and the solid state spectrum of the $Cr_3(\mu_3\text{-}O)$-glycine complex exhibit two main bands, one at 585 nm and the other at 434 nm (see Table II). These are assigned by Dubicki and Martin [17], in their detailed study of the isostructural $Cr_3(\mu_3\text{-}O)$-carboxylate systems, to be the spin-allowed 3d–3d transitions of the octahedrally surrounded Cr(III) ions. The $Cr_3(\mu_3\text{-}O)$ trimer structure is characterised, however, by a pronounced shoulder at 666 nm and a weak absorption at 712 nm. A similarity between the glycinate and carboxylate

TABLE II. Solid-State and Solution (EtOH) Spectral Data (nm) for $Cr_nFe_{3-n}(\mu_3\text{-}O)$-Glycinate Complexes.

	Band 1	Band 2	Weak Bands			
$Fe_2Cr(\mu_3\text{-}O)$-glycinate	500 nm	442 nm	645	685	695	720
$Cr_2Fe(\mu_3\text{-}O)$-glycinate	510	444	645	685	695	720
$Cr_3(\mu_3\text{-}O)$-glycinate	585	434	666	–	–	712
$Cr_3(\mu_3\text{-}O)$-acetate (Dubicki's results [17])	579	437	660	–	–	710

spectra is to be expected, since both are co-ordinated via the $-CO_2$ group, and we see no reason to alter the interpretation proposed by the previous authors.

The most notable feature of the spectra for both the mixed-metal trinuclear μ_3-oxo bridged glycinate species is the absence of the pronounced charge-transfer band which is characteristic for $Fe_3\text{-}(\mu_3\text{-}O)$ complexes. The resulting spectra resemble those of the $Cr_3\text{-}(\mu_3\text{-}O)$ system in clarity, but the bands are shifted considerably in position. One of the two main bands of the $Cr_3\text{-}(\mu_3\text{-}O)$ complex remains unchanged at *ca.* 440 nm for the mixed Fe/Cr complexes but the other is shifted to *ca.* 500 nm. There are also four weak bands observed at 720, 695, 685 and 645 nm but their origin remains undetermined.

Although there have been few reports in the literature of O–O bridged amino-acid trinuclear complexes, our experience with the preparation of the series reported here suggests that they are no more difficult to prepare than the analogous carboxylate trimers. In these preparations we have found that the formation of the trimer in solution is readily monitored (except for the $Fe_3\text{-}(\mu_3\text{-}O)$ complex) using the characteristic bands in the visible spectrum referred to earlier. Published preparative methods for the carboxylates [18] are often lengthy and one is tempted to infer that the trinuclear skeleton forms very slowly. On the contrary, the characteristic bands in the visible spectrum indicate that the trinuclear skeleton is present as soon as the metal salt has completely dissolved in the appropriate carboxylate or glycinate solution. We have confirmed this by immediate precipitation of the trinuclear complex from solution with the addition of a suitable solvent mixture (*e.g.* acetone/ether) using the visible spectrum as a diagnostic aid in the preparation of the mixed $Cr_nFe_{3-n}\text{-}(\mu_3\text{-}O)$ glycinate series, we have shown that the formation of the $Fe_3\text{-}(\mu_3\text{-}O)$ trimer predominates in aqueous solution to the exclusion of the formation of the mixed Fe/Cr species. An ethanolic medium is necessary for the incorporation of Cr(III), just as it is for the formation of the $Cr_3\text{-}(\mu_3\text{-}O)$ complex. This is also consistent with previous observations for dimeric Cu(II) systems [19], where ethanolic solutions were found to encourage the formation of O–O bridged amino-acid complexes.

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References

1 J. Catterick and P. Thornton, *Adv. Inorg. Chem. Radiochem., 20,* 291 (1977).
2 R. Weinland and E. Gussmann, *Ber. Dtsch. Chem. Ges., 42,* 3881 (1909).
3 A. B. Black, A. Yavari and H. Kubicki, *J. Chem. Soc. Chem. Commun.,* 796 (1981).
4 A. Chretien and E. Lous, *Bull. Soc. Chim. Fr., 11,* 446 (1944).
5 F. A. Cotton and W. Wang, *Inorg. Chem., 21,* 2675 (1982).
6 F. A. Cotton and J. G. Norman Jr., *Inorg. Chim. Acta, 6,* 411 (1972).
7 A. R. E. Baikie, M. B. Hursthouse, D. B. New and P. Thornton, *J. Chem. Soc., Chem. Commun.,* 62 (1978).
8 E. C. Devore, S. L. Holt, R. O. Asplund and A. W. Catalano, *Arch. Biochem. Biophys., 146,* 659 (1971).
9 R. N. Puri and R. O. Asplund, *Inorg. Chim. Acta, 54,* L187 (1981).
10 Y. V. Rakitin, T. A. Zhemchuzanikova and V. V. Zelentsov, *Inorg. Chim. Acta, 23,* 145 (1977).
11 W. Clegg, O. M. Lam and B. P. Straughan, *Angew. Chem., 23,* 434 (1984).
12 M. Tsuboi, K. Onishi, I. Nakagawa, T. Shimanouchi and S. Mizushima, *Spectrochim. Acta, 12,* 253 (1958).
13 G. B. Deacon and R. J. Philips, *Coord. Chem. Rev., 33,* 227 (1980).
14 E. M. Holt, S. L. Holt, W. F. Tucker, R. O. Asplund and K. J. Watson, *J. Am. Chem. Soc., 96,* 2621 (1974).
15 M. K. Johnson, R. D. Cannon, D. B. Powell, *Spectrochim. Acta, Part A, 38,* 307 (1982).
16 R. N. Puri and R. O. Asplund, *Inorg. Chim. Acta, 66,* 49 (1982).
17 B. L. Dubicki and R. L. Martin, *Aust. J. Chem., 22,* 701 (1969).
18 B. N. Figgis and G. B. Robertson, *Nature, 205,* 694 (1965).
19 T. Glowiak and H. Kozlowski, *Inorg. Chim. Acta, 46,* L65 (1980).