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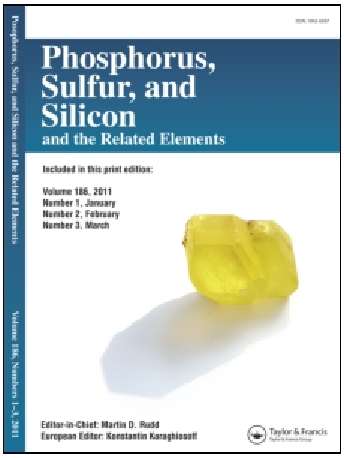

Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
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To cite this Article Veltsistas, Panagiotis , Papadimitriou, Christos , Arabatzis, Yannis , Slawin, Alexandra M. Z. and Woollins, J. Derek(1997) 'Oxamate and Chloranilate Bridges in Polymeric Networks', Phosphorus, Sulfur, and Silicon and the Related Elements, 124: 1, 407 — 411

To link to this Article: DOI: 10.1080/10426509708545648

URL: http://dx.doi.org/10.1080/10426509708545648

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Phosphorus, Sulfur, and Silicon, 1997, Vol. 124 & 125, pp. 407–411
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OXAMATE AND CHLORANILATE BRIDGES IN POLYMERIC NETWORKS

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Abstract: Oxamic acid acts as a bridging ligand with lanthanide ions to form, for example 9-coordinate Ho(III) systems in which the holmium centres are linked into sheets via H-bonds. Nd(III) also forms 9-coordinate complexes with oxamate but an alternative packing motif is observed. Multidentate ligands such as chloroanilate can also induce interesting networks. Thus with sodium and phenanthroline a complex which contains 7-coordinate sodium atoms linked together to form infinite double chains is observed.

Keywords: supramolecular structures; holmium; neodymium, sodium, oxamate; chloroanilate.

INTRODUCTION

The coordination chemistry of multidentate ligands provides an easy entry into extended supramolecular arrays. Amongst ligands suitable for this type of application is oxalate which has been extensively studied. Here we report on the related oxamate coordination to holmium and neodymium. Furthermore we describe a novel structure for a chloroanilate complex of sodium.

Thus, for the synthesis of the lanthanide compounds we simply took a silicate (water glass) solution and added it to oxamic acid until the pH reached ca 5. After settling in a glass column for two days a solution of MCl_3 was allowed to diffuse slowly through the gel and react with the anionic ligand. The periodic spatially ordered precipitation (Liesegang rings) were evident at the top of the column while the insoluble product grew in crystalline form in the lower levels of the gel. The vibrational spectra of the $[Ho(oxam)_3(H_2O)_3]_4 2.75H_2O$ **1** and $Nd(oxam)_4]2.5H_2O$ **2** were as anticipated with complex high frequency regions as a consequence of H-bonding. In their X-ray structures both have nine-coordinate core geometry; in **1** this is made up (Fig. 1) of three bidentate oxamate ligands and three coordinated water molecules whereas in **2** (Fig. 2) the coordination is due to entirely to oxamate coordination – three bidentate and one tridentate bridging.

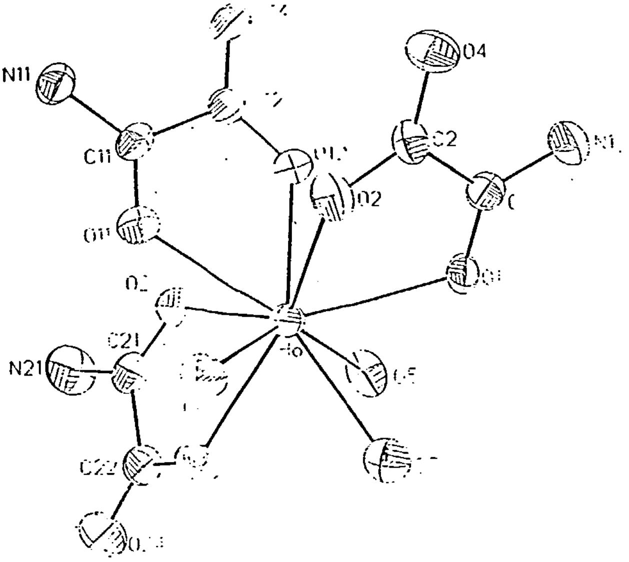

FIGURE 1 Core geometry in $[Ho(oxam)_3(H_2O)_3]_4.2.75H_2O$

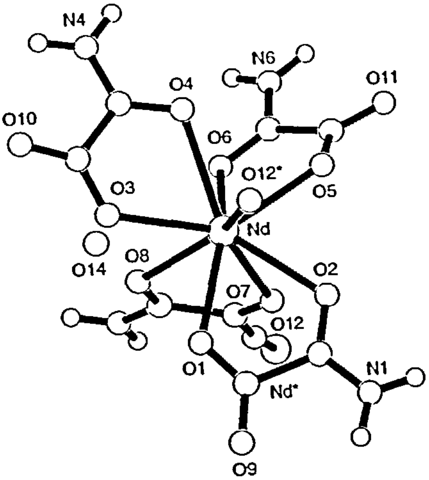

FIGURE 2 Core geometry in $Nd(oxam)_4].2.5H_2O$

In 1 the Ho centre is in an approximately tricapped trigonal prismatic geometry. Hydrogen bonding involving water molecules connects two carboxylic oxygen atoms O(1) and O(14) to give (fig. 3) infinite chains of holmium-oxamates running perpendicular to the *b* direction. These chains are held together by H-bonds to form sheets.

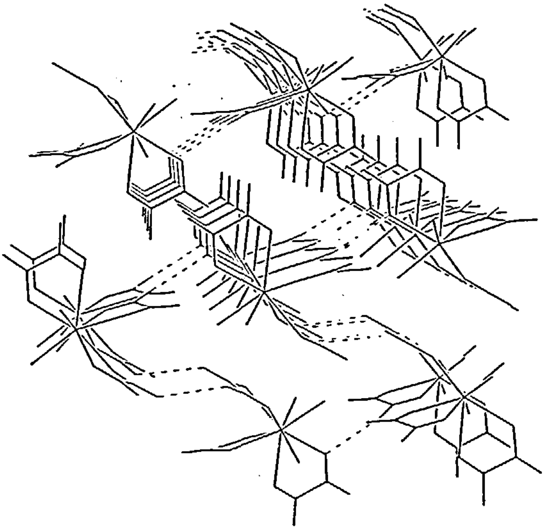

FIGURE 3 Sheet Structure in $[Ho(oxam)_3(H_2O)_3]_4.2.75H_2O$

In contrast to **1** the Nd in **2** is in an approximately C_{4v} geometry. The molecules pack with one oxamate being tricoordinate thus forming chains. There are a number of intramolecular H-bonds within these chains but no evidence of sheet formation (Fig. 4).

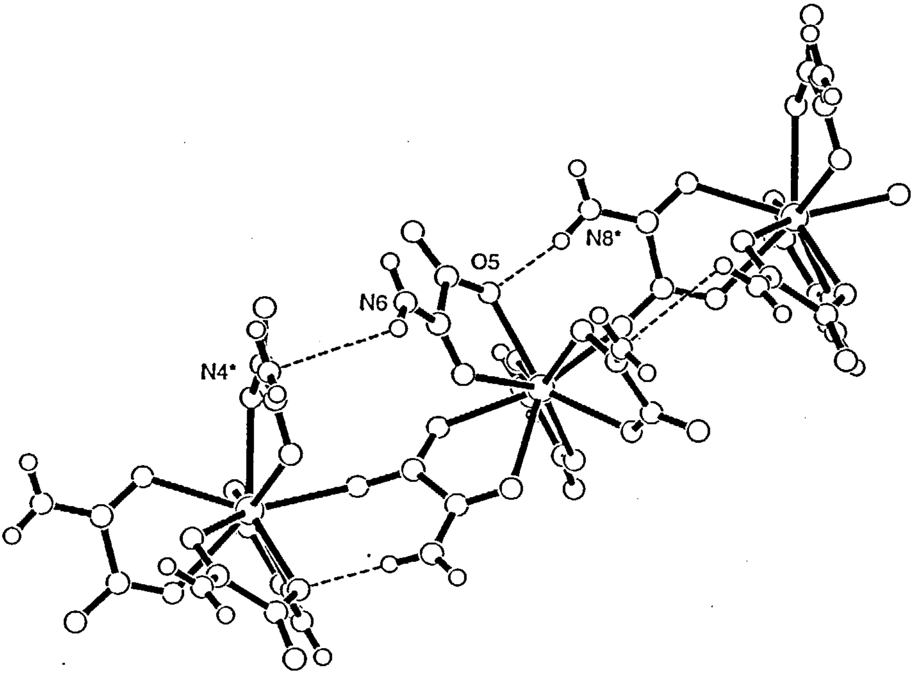

FIGURE 4 Chain Structure in Nd(oxam)$_4$].2.5H_2O

In a similar methodology to that for **1** and **2** we have found that crystallisation of phenanthroline, NaOH and chloroanilate gives [Na_2(phen)(ac)].$2H_2O$ **3**. In **3** both sodium cations are 7-coordinate, with the dinuclear unit being H-bonded to adjacent molecules to form infinite double chains which are interlinked by H-bonds (Fig. 5).

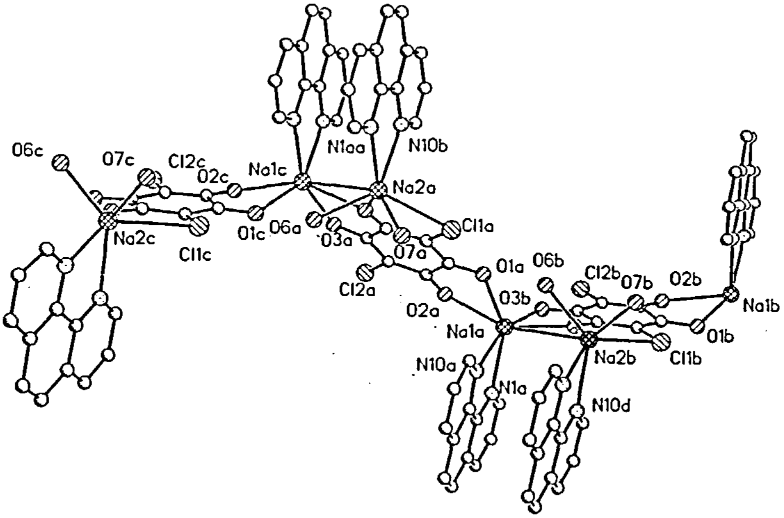

FIGURE 5 Chain Structure in $[Na_2(phen)(ac)].2H_2O$

Apart from X-ray and vibrational spectroscopic studies we have also investigated the thermal properties of **1-3**. For both **1** and **2** the tga curves reveal that the final products are the metal oxides.