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COMMUNICATION

SYNTHESIS AND X-RAY STRUCTURE OF AN (OXAMATO)PRASEODYMIUM POLYMER, $[Pr(HNCOCO_2)_{1.5}(H_2O)_3]_n \cdot 2.75H_2O$

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Abstract—Gel crystallisation of oxamic acid with praseodymium nitrate hexahydrate gave the title compound which has an essentially rigid sheet polymer structure comprised of fused 24-membered metallocycle rings. Upon thermal decomposition the polymer gives Pr_6O_{11}.

Oxamic acid may act as a bidentate, tridentate or tetradentate (bridging) ligand in a number of coordination modes both as a mono and as a dianion.[1–3] A number of interesting species containing bridging oxamate have been described, for example "platinum oxamate blue"[4] and exchange-coupled binuclear systems.[5] Oxalate complexes have also been shown to support polymeric structures and have potential as molecular-based ferromagnets.[6] We are investigating the usefulness of oxamate as a bridging ligand for the formation of new coordination polymers. Thus, slow diffusion of praseodymium nitrate solution into oxamic acid contained in a water glass gel gave **1** as a pale green crystalline solid.

The X-ray structure† of **1** shows the praseodymium to be coordinated (Fig. 1) by three bidentate oxamato ligands and three water molecules in a tricapped trigonal prismatic nine-coordination geometry. The capping atoms are from oxamato ligands and the water molecules occupy some of the vertices of the trigonal prism. The Pr—O aquo

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† *Crystal data*: $C_3H_{13}N_{1.5}O10.25$ Pr: monoclinic, space group $P2_1/a$, $a = 10.386(4)$, $b = 9.594(3)$, $c = 11.304(4)$ Å, $\beta = 115.28(3)°$, $U = 1018$ Å^3, $D_c = 2.45$ g cm^{-3}, $F(000) = 730$, $\mu(\text{Mo-}K_\alpha) = 48.3$ cm^{-1}. A total of 2974 independent reflections were collected using a Siemens *P*4/PC diffractometer with graphite monochromated Mo-K_α radiation and ω scans. The structure was solved by direct methods and refined anisotropically to give $R = 3.37$ and $R_w = 4.04\%$ for 2860 independent observed, absorption corrected reflections. The oxamato ligand is disordered with each coordinating atom having an occupancy of 0.25(NH) and 0.75(O); the structure was refined using O atoms in all of these sites.

Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See information for Authors Issue No. 1.

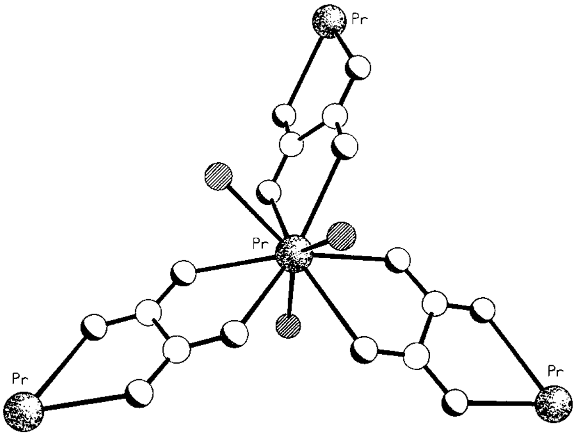

Fig. 1. The praseodymium coordination geometry in the X-ray structure of **1**. The fully hatched atoms represent the aquo oxygens and the partially hatched atoms, the O/N atoms of the oxamato ligands. The Pr—O/N distances are in the range 2.473(4)–2.577(5) Å and the Pr—O (aquo) distances are in the range 2.507(5)–2.533(6) Å.

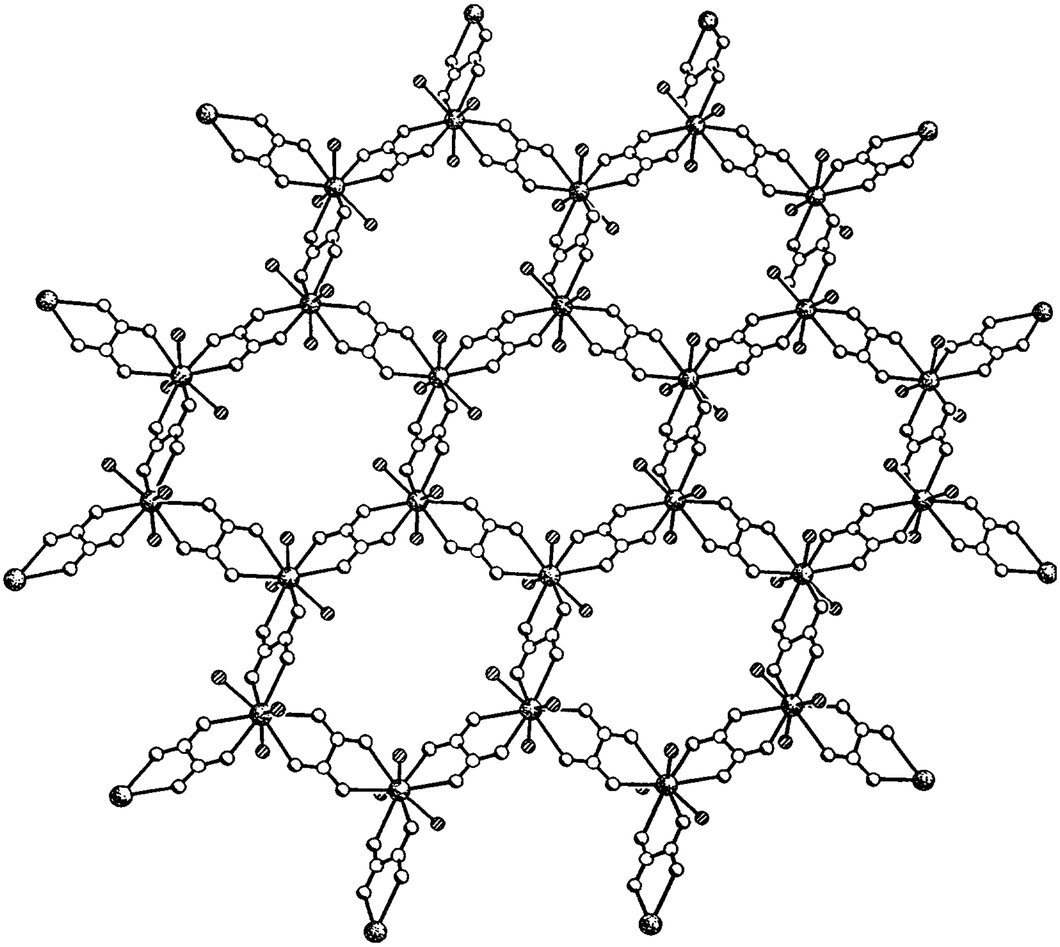

Fig. 2. Part of one of the sheets of contiguous 24-membered metallacycles in the crystals of **1**.

distances are in the range 2.507(5)–2.533(6) Å and the Pr—O/N oxamato‡ distances lie between 2.473(4) and 2.577(5) Å whilst the ranges for the C—O/N and C—C bond lengths are 1.239(5)–1.270(7) and 1.548(8)–1.556(10) Å respectively.

The oxamato ligands serve to bridge adjacent Pr-centres forming a series of contiguous 24-membered metallacycles (Fig. 2), each containing six praseodymium atoms and six oxamato ligands. The metallacycles form close to planar sheets (the Pr atoms, which have separations of 6.46 and 6.59 Å, lie ±0.5 Å above and below the mean plane are arranged in a pseudo chair "cyclohexyl"-like array) that extend in the crystallographic *a* and *c* directions. Adjacent sheets, in the *b* direction, are offset with respect to each other such that one of the oxamato C—C bonds in one sheet lies approximately over the centre of the metallacyclic ring of the next sheet, the mean intersheet separation is *ca* 4.8 Å. The solvate water molecules are situated in a series of partial occupancy sites in between the polymeric sheets. Although the aquo and water hydrogen atoms could not be located there is clearly an extensive hydrogen bonding network; it is to be expected that variable amounts of solvate water could be trapped within the lattice.

The diffuse reflectance spectrum of **1** [446(s), 471(s), 485(s), 591(s), 601(sh) nm] is, as expected, similar to that observed[7] for $K_3[Pr(HNCCO_2)_3(H_2O)_3]$ and is consistent with the presence of Pr^{III}. The vibrational spectrum of **1** contains§ the expected ν(NH) and ν(OH) vibrations together with amide and CO^{2-} group vibrations. In particular, a strong broad doublet [ν(CO)] at *ca* 1620 cm^{-1} is indicative of bridging oxamato groups.[8]

Thermogravimetric, differential thermal analysis and differential thermal gravimetric studies on **1** reveal an exotherm that begins at 83°C and finishes with a strong peak at 126°C (11.2% weight loss) corresponding to loss of ammonia [eq. (1)]. There is a further exotherm at 385°C followed by an endothermic process at 424°C which, from weight loss, leads to the overall formation of Pr_6O_{11}¶

$$[Pr_2(HNCOCO_2)_3(H_2O)_6]5.5H_2O \rightarrow [Pr_2(O_2CCO_2)_3(H_2O)_3]5.5H_2O + 3NH_3. \quad (1)$$

The ease of synthesis coupled with the structure observed for **1** suggests the possibility for the formation of a series of new polymeric materials which are capable of trapping small molecules and may act as precursors to metal oxides.

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‡ The polymeric nature of the structure and the presence of centres of symmetry at the middle of the C—C bonds in the oxamato ligands necessitate that within each ligand the nitrogen atom is disordered over all four sites. All sites have been refined as O atoms and bondlengths do not indicate any degree of preferred ordering.

§ Important vibrations: ν(NH) IR: 3388, 3240; Raman 3408, 3244 cm^{-1}; ν(CO) IR: 1683, 1641, 1608; Raman 1646 cm^{-1}; CO_2-group IR: 1402, 1319 cm^{-1}.

¶ Microanalytical and spectroscopic data are in accord with the formulation as Pr_6O_{11}.

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