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When is a reported air-stable Pr^{IV} complex not a Pr^{IV} complex? Answer: when it is Pr^{III}

Zhifang Guo^a, Glen B. Deacon^b  and Peter C. Junk^a 

^aCollege of Science and Engineering, James Cook University, Townsville, Queensland, Australia;

^bSchool of Chemistry, Monash University, Clayton, Victoria, Australia

ABSTRACT

All the data recently reported for the purported air/water stable Pr^{IV} complex, [(L)Pr^{IV}(L)₄(OH_{0.94}Cl_{0.06})₂Pr^{IV}(L)]_n (L = *N*-acetylanthranilate) [1], have been reinterpreted to show that it is, in fact, the Pr^{III} complex [Pr₂L₆(H₂O)₂]_n. Importantly, it is isomorphous with its reported Eu^{III} analogue [Eu₂L₆(H₂O)₂]_n [2], providing further evidence of the incorrect assignment in the literature.

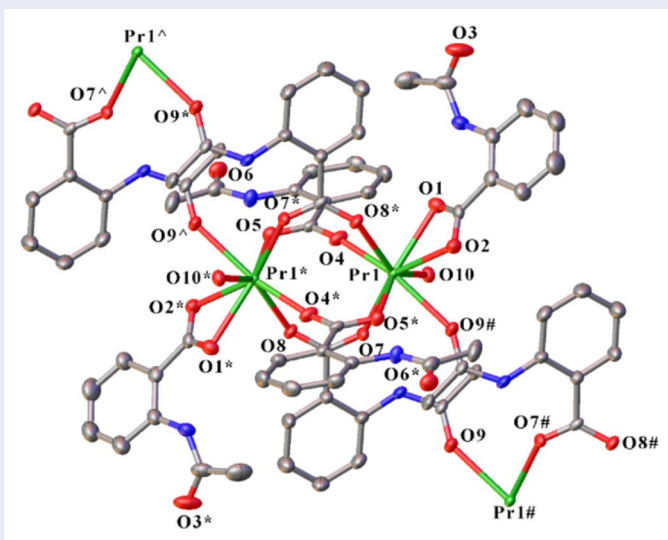
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CONTACT Peter C. Junk  peter.junk@jcu.edu.au  College of Science and Engineering, James Cook University, Townsville, QLD, 4811, Australia

This paper is dedicated to Professor Jim Atwood on his retirement. Jim made some outstanding contributions to organometallic and coordination chemistry and has been a great colleague and friend. His contribution as Edition-Chief to this journal has been epic.

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1. Introduction

Among the many exciting developments in rare earth chemistry in recent decades are the preparations of molecular complexes in unusual oxidation states. A major achievement has been the extension of the divalent oxidation state from the traditional Sm, Eu, and Yb to all the elements except Pm [3, 4]. More recently, notably in work by Mazzanti and La Pierre, molecular Pr^{IV} and Tb^{IV} complexes have been prepared [5–15], these oxidation states having been previously accessed only in oxides and fluorides [16]. There have been further elaborations of Pr^{IV} silyloxy in complexes by Zheng [17, 18]. All these syntheses and handling of products required the use of inert atmosphere conditions because of the instability of the Ln^{IV} complexes to air and moisture. Consequently, we were surprised or even astonished to read a report of an air and water-stable Pr^{IV} coordination polymer, [(L)Pr^{IV}(L)₄(OH_{0.94}Cl_{0.06})₂Pr^{IV}(L)] (L = *N*-acetyl-anthranilate), and its anti-proliferative activity against several cancer cell lines [1]. This has led us to re-refine the reported data and we find that it can be satisfactorily fitted to a Pr^{III} polymer with the composition [Pr₂L₆(H₂O)₂]_n, which also is consistent with the reported microanalysis for the bulk product and accords with the air and water stability. Furthermore, there is a reported Eu^{III} complex of the *N*-acetyl anthranilate ligand [2] that is isomorphous with the Pr complex.

2. Discussion

Table 1 compares the reported refinement as a Pr^{IV} complex [1] with our refinement as [Pr₂L₆(H₂O)₂]_n and the reported [Eu₂L₆(H₂O)₂]_n [2]. As is evident, the solution as a trivalent complex is at least as satisfactory as that reported with the additional advantage of explaining the air and water stability. Our structure based on the new refinement is shown in Figure 1. The complex is a polymer of centrosymmetric dimeric units in which Pr^{III} is eight-coordinate, with one chelating carboxylate, four oxygen atoms

Table 1. Crystal data and structural refinement for the reported Pr^{IV} complex, as a Pr^{III} [Pr₂L₆(H₂O)₂]_n complex and the reported Eu^{III} complex.

	Pr ^{IV} (CCDC 2075265) [(L)Pr ^{IV} (L) ₄ (OH _{0.94} Cl _{0.06}) ₂ Pr ^{IV} (L)] _n	Pr ^{III} [Pr ₂ L ₆ (H ₂ O) ₂] _n	Eu ^{III} (CCDC 674226) [Eu ₂ L ₆ (H ₂ O) ₂] _n
Formula	C ₂₇ H _{24.93} N ₃ O _{9.94} PrCl _{0.07}	C ₂₇ H ₂₆ N ₃ O ₁₀ Pr	C ₂₇ H ₂₆ EuN ₃ O ₁₀
<i>M_r</i>	693.61	693.42	704.47
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	10.787(4)	10.787(4)	10.7419(10)
<i>b</i> (Å)	10.726(3)	10.726(3)	10.6339(9)
<i>c</i> (Å)	24.591(8)	24.591(8)	24.967(2)
α (°)	90	90	90
β (°)	98.646(7)	98.646(7)	100.2610(10)
γ (°)	90	90	90
<i>V</i> (Å ³)	2812.9(15)	2812.9(15)	2806.3(4)
<i>Z</i>	4	4	4
ρ _{calc} , g cm ⁻³	1.638	1.637	1.667
μ, mm ⁻¹	1.799	1.793	2.296
<i>N_t</i>	51228	51248	15785
<i>N</i> (<i>R_{int}</i>)	7483 (0.1579)	7486 (0.1579)	5696 (0.0235)
<i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>))	0.0559	0.0557	0.380
<i>wR</i> ₂ (all data)	0.1454	0.1377	0.1637
<i>GOF</i>	1.060	1.027	1.174

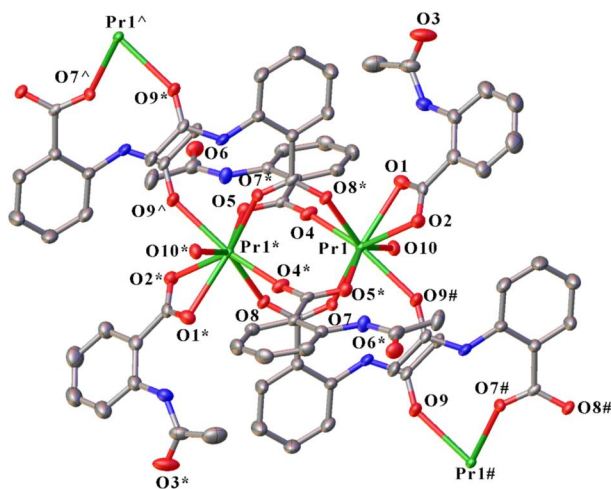


Figure 1. Crystal structure of the Pr^{III} complex [Pr₂L₆(H₂O)₂]_n (symmetry code: *1 - X, 1 - Y, 1 - Z; #1 - X, -Y, 1 - Z; ^+X, 1 + Y, +Z). Hydrogen atoms were omitted for clarity.

from four bridging bidentate carboxylates, one coordinated acetyl oxygen, and one water molecule. The acetyl oxygen is from a ligand separate from those of the dimeric unit and hence this linkage builds the dimers into a polymer.

A key difference between the Pr^{IV} and the Pr^{III} structures is that the former has a disordered Pr-OH/Cl (94/6%), while the latter has a Pr-OH₂ bond. The Pr-OH₂ bond length (2.477(3) Å) lies within the range 2.44–2.62 Å for 18 examples of eight-coordinate complexes with Pr^{III}-OH₂ bonds listed in the CCDC [19]. On the other hand, this distance (2.477(3) Å) is far too long for a terminal Pr^{IV}-OH bond. There are only two terminal Pr^{III}-OH bonds in the CCDC, 2.257 Å [20] and 2.373 Å [21], and Pr^{IV}-OH bonds should be 0.16 Å shorter than Pr^{III}-OH [22], *i.e.* 2.21–2.09 Å. O10 from the terminal water forms hydrogen bonds to two neighboring O atoms, O6& (-x, 1 - y, 1 - z) and O3\$(1/2 - x, y - 1/2, 1/2 - z), consistent with coordination of water and not OH (Figure 2).

The Pr-O(carboxylate) bond lengths (Table 2) are also appropriate for chelating and bridging bidentate carboxylatopraseodymium(III) complexes (*e.g.* [Pr(4-HOC₆H₄COO)₃(H₂O)(DMF)]₂(DMF)₃ [23], [Pr₂(aip)₃(H₂O)₂·3H₂O]_n (aip = 5-aminoisophthalate) [24]), but are significantly longer than would be expected for Pr^{IV} analogues. Likewise binding of the acetyl group Pr-O9 (Table 2) is also appropriate for a Pr^{III} complex with a bond length close to that of Pr^{III}-OH₂. Comparing the bond lengths with those of the isomorphous Eu^{III} complex (Table 1) shows that the bond length difference for the chelating carboxylate and the coordinated water is near the 0.06 Å expected from ionic radius values [22]. The differences for the Ln-O(bridging carboxylate) bond lengths are much more variable and the average is less than expected, perhaps pointing to increased steric strain with the smaller Eu. On the other hand, the coordinated carbonyl oxygen is more distant than expected in the Pr complex.

About bulk composition, the observed microanalysis values [1] C, 46.63; H, 3.71; N 5.99% fit [Pr₂L₆(H₂O)₂]_n, C₅₄H₅₂N₆O₂₀Pr₂ calc.: C 46.77; H, 3.78; N 6.06%, as well as for the Pr^{IV} formulation, calc. C, 46.76; H, 3.63; N, 6.06%. Regarding the reported ¹H NMR

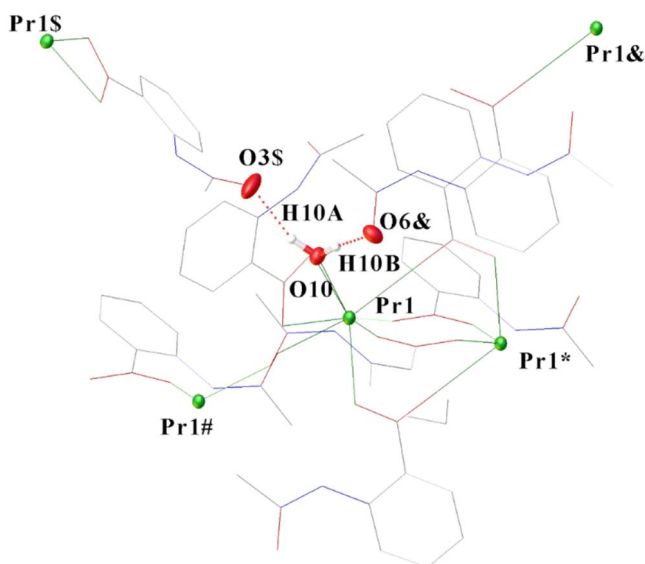


Figure 2. H-Bond formation from O10 of coordinated water to two neighboring oxygen atoms. H10B–O6& ($-x, 1 - y, 1 - z$) 1.895(4) Å; H10A–O3\$ ($1/2 - x, y - 1/2, 1/2 - z$) 1.851(4) Å. O10–H10B–O6& 171.7(3)°, O10–H10A–O3\$ 158.3(3)°.

Table 2. Bond lengths (Å) for the reported Pr^{IV} complex, as a Pr^{III} complex [Pr₂L₆(H₂O)₂]_n and the reported Eu^{III} complex.

	Pr ^{IV} (CCDC 2075265) [(L)Pr ^{IV} (L) ₄ (OH) _{0.94} Cl _{0.06}] ₂ Pr ^{IV} (L)] _n	Pr ^{III} [Pr ₂ L ₆ (H ₂ O) ₂] _n	Eu ^{III} (CCDC 674226) [Eu ₂ L ₆ (H ₂ O) ₂] _n
Ln1–O1	2.494(4)	2.494(4)	2.444(4)
Ln1–O2	2.546(4)	2.545(4)	2.489(4)
Ln1–O4	2.414(4)	2.416(3)	2.336(4)
Ln1–O7	2.416(4)	2.418(3)	2.447(3)
Ln1–O5*	2.443(4)	2.443(4)	2.489(4)
Ln1–O8*	2.434(3)	2.435(3)	2.362(4)
Ln1–O9#	2.487(4)	2.485(3)	2.384(4)
Ln1–O10	2.487(10)	2.477(3)	2.431(4)
Ln1–Cl1	2.47(4)		

assignments [1], most apply equally well to the present structural proposal, except that 14.79 ppm, assigned to Pr–OH, was an unlikely attribution owing to exchange with water in the d₆-dmsO solvent. If 10.54 ppm is assigned to NH of the uncoordinated N-acetylamido group, 14.75 ppm may be assigned to NH of the coordinated-acetylamido group, paramagnetic shifted by Pr^{III}. The pale green color of the complex [1] is as expected for Pr³⁺, while a broad ligand absorption at 305 nm obscures any f-f transitions, which are of low intensity [1]. The reported TGA [1] shows a weight loss of 2.47% below 200 °C, which can be attributed to loss of coordinated water before more substantial decomposition above 200 °C. The broad features in the IR spectrum from 3250 to 2550 cm⁻¹ can encompass OH stretching of coordinated water as well as extensive NH stretching. Carboxylate absorptions are similarly assigned for either structure, though the use of KBr disks raises the possibility of carboxylate exchange giving KL and Pr bromide species [25]. The reported magnetic moment of 2.8 B.M. is low for Pr^{III} [26], but not unknown [27]. Further, with errors in oxidation state and

composition, the diamagnetic correction will be wrong. Accordingly, all the reported data for the reported Pr^{IV} polymeric complex can be accommodated with it being the Pr^{III} complex [Pr₂L₆(H₂O)₂]_n.

3. Conclusion

The reported air stable Pr^{IV} complex, [[(L)Pr^{IV}(L)₄(OH_{0.94}Cl_{0.06})₂Pr^{IV}(L)]_n (L = *N*-acetyl-anthranilate), is in reality a Pr^{III} complex [Pr₂L₆(H₂O)₂]_n.

4. Experimental

The X-ray crystal structure of the reported Pr^{IV} complex (CCDC 2075265) was downloaded from the CCDC database, and res/hkl files were extracted from the cif file in Olex2 [28]. The structure was solved and refined by SHELXT and SHELX2015 [29]. Crystal data and refinement details are given in Table 1. CCDC 2355887 for the Pr^{III} compound reported here contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Disclosure statement

No potential conflict of interest was reported by the authors.

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ORCID

Glen B. Deacon  <http://orcid.org/0000-0002-6966-6121>

Peter C. Junk  <http://orcid.org/0000-0002-0683-8918>

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