Volume 26
Number 26
December 30, 1987

Inorganic Chemistry

Communications

$A_2Ln_2Ti_3O_{10}$ (A = K or Rb; Ln = La or Rare Earth): A New Series of Layered Perovskites Exhibiting Ion Exchange

Sir:

There is considerable interest at present in layered transition-metal oxides built of metal–oxygen octahedra where the interlayer positions are occupied by large alkali-metal atoms.[1,2] Oxides of this type exhibit ion exchange (of the interlayer cations) and intercalation properties. Two types of layered oxides derived from the perovskite (ABO_3) structure are known. One is the Ruddlesden–Popper series[3] of the general formula $A_2[A_{n-1}B_nO_{3n+1}]$ where $[A_{n-1}B_nO_{3n+1}]$ perovskite-like slabs of n octahedra in thickness, formed by slicing the perovskite structure along one of the cubic directions, are interleaved by A cations. Sr_2TiO_4, $Sr_3Ti_2O_7$, and $Sr_4Ti_3O_{10}$ are well-known examples of this family. Layered oxides of the type $KCa_2Nb_3O_{10}$ reported by Dion et al.[4] are similar to the Ruddlesden–Popper series, where the interlayer cation density is only 50% of that in the Ruddlesden–Popper series. The latter series may be represented by the general formula $A^1[A'_{n-1}B_nO_{3n+1}]$ where A^1 is an alkali-metal cation. Unlike the Ruddlesden–Popper series, $A^1[A'_{n-1}B_nO_{3n+1}]$ exhibit ion exchange and intercalation behavior[2,5,6] owing to the lesser interlayer charge density. We expected that appropriately tailored Ruddlesden–Popper series of oxides containing alkali-metal ions in the interlayer region would exhibit ion exchange and intercalation chemistry. Our expectation is based on the fact that ion-exchange reactions are quite a widespread phenomenon in inorganic oxides even where the diffusion coefficients of the exchangeable cations are small ($D \sim 10^{-11}$ cm^2 s^{-1}).[7] Accordingly, we report in this communication the synthesis of a new series of layered perovskites of the general formula $A_2[Ln_2Ti_3O_{10}]$ (A = K, Rb; Ln = La, Nd, Sm, Gd, Dy) exhibiting facile ion exchange of the alkali metal in aqueous or molten salt media. Of special interest is the proton exchange of these oxides, yielding a new family of protonated oxides, $H_2Ln_2Ti_3O_{10}$, that retain the parent layered structure. The lanthanum compound of this family, $H_2La_2Ti_3O_{10}$, dehydrates to give a new defective cubic perovskite, $La_{2/3}TiO_3$.

Table I. Tetragonal Lattice Parameters of $K_2Ln_2Ti_3O_{10}$ and $K_2Ln_2Ti_3O_{10}{\cdot}H_2O$[a]

	anhydrous		hydrate	
Ln	a, Å	c, Å	a, Å	c, Å
La	3.871 (2)	29.78 (2)	3.862 (4)	16.85 (2)
Nd	3.852 (4)	29.61 (3)	3.843 (3)	16.68 (2)
Sm	3.842 (8)	29.61 (6)	3.820 (6)	16.82 (3)
Gd	3.836 (9)	29.64 (7)	3.819 (11)	16.70 (5)
Dy	3.811 (8)	29.70 (7)	3.800 (7)	16.69 (4)

[a] Rb analogues exist for Ln = La and several rare earths. For example, anhydrous $Rb_2La_2Ti_3O_{10}$ is tetragonal with a = 3.898 (3) and c = 30.50 (2) Å.

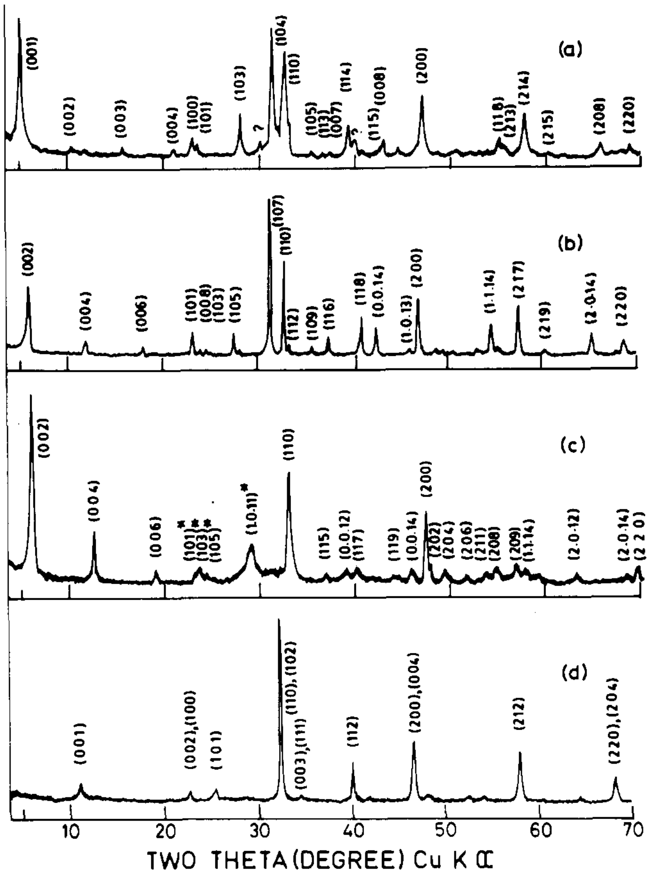

Figure 1. X-ray powder diffraction patterns of (a) $K_2La_2Ti_3O_{10}{\cdot}H_2O$, (b) $K_2La_2Ti_3O_{10}$, (c) $H_2La_2Ti_3O_{10}$, and (d) $La_{2/3}TiO_3$. Reflections with asterisks in (c) are indexed with a doubled c; i.e., c = 55.3 Å.

$A_2Ln_2Ti_3O_{10}$ were prepared by heating appropriate mixtures of A_2CO_3, Ln_2O_3, and TiO_2 in air at 1000 °C for 2 days with one grinding in between. Excess A_2CO_3 (~20 mol %) was added to

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(7) England, W. A.; Goodenough, J. B.; Wiseman, P. J. *J. Solid State Chem.* **1983**, *49*, 289.

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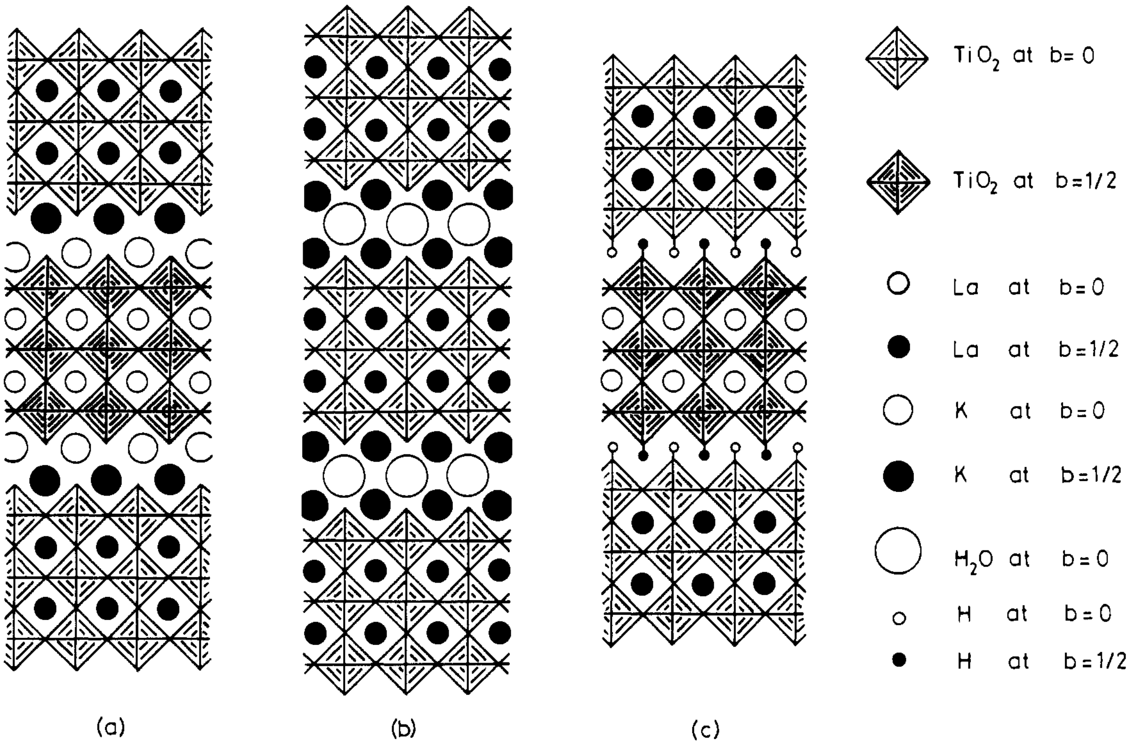

Figure 2. Schematic representation of the structures of (a) $K_2Ln_2Ti_3O_{10}$, (b) $K_2Ln_2Ti_3O_{10}{\cdot}H_2O$, and (c) $H_2Ln_2Ti_3O_{10}$.

Table II. Tetragonal Lattice Parameters of $H_2Ln_2Ti_3O_{10}$

compd	*a*, Å	*c*, Å
$H_2La_2Ti_3O_{10}$	3.820 (9)	27.66 (7)
$H_2Sm_2Ti_3O_{10}$	3.780 (13)	26.75 (9)
$H_2Gd_2Ti_3O_{10}$	3.768 (7)	26.61 (5)
$H_2Dy_2Ti_3O_{10}$	3.755 (7)	26.48 (5)

compensate for the loss due to volatilization. After the reaction, the products were washed with distilled water and dried at 500 °C to obtain the anhydrous oxides. These compounds are hygroscopic, forming hydrates, $A_2Ln_2Ti_3O_{10}{\cdot}H_2O$, on exposure to air. Lattice constants of the newly synthesized oxides and their hydrates are listed in Table I. Both anhydrous and hydrated oxides crystallize in tetragonal structure similar to $Sr_4Ti_3O_{10}$[3] (Figure 1); the *c* parameter is however halved on hydration. The anhydrous compounds are likely to possess the *I4/mmm* space group, while the hydrated compounds may belong to *P4/mmm* symmetry.

By analogy with the structures of $Sr_4Ti_3O_{10}$[3] and A $Ca_2Nb_3O_{10}$,[8] the structure of $A_2Ln_2Ti_3O_{10}$ may be visualized as consisting of three-octahedra-thick perovskite slabs, $[Ln_2Ti_3O_{10}]$, stacked one over the other, with the alkali-metal atoms occupying interlayer positions (Figure 2a). The *c* parameter (~30 Å) is indicative of a displacement of adjacent perovskite slabs by $(a + b)/2$, exactly as in the structure of $Sr_4Ti_3O_{10}$. The absence of *c*-axis doubling in the hydrated oxides indicates the stacking of adjacent slabs without relative displacement (Figure 2b).

The interlayer potassium ions in $K_2Ln_2Ti_3O_{10}$ are easily exchanged with Na^+ and Li^+ by treating the solids with molten alkali-metal nitrates.[9] The ion-exchanged products retain the parent structure. More importantly, $K_2Ln_2Ti_3O_{10}$ readily exchanges K^+ with H^+ on treatment with dilute acids,[10,11] giving $H_2Ln_2Ti_3O_{10}$. X-ray diffraction data reveal that the protonated oxides retain the parent structure of $K_2Ln_2Ti_3O_{10}$ except for a small decrease in the *c* parameter (Table II). This is to be contrasted with $KCa_2Nb_3O_{10}/HCa_2Nb_3O_{10}$, where proton exchange is accompanied by a relative displacement of perovskite slabs.[5] A schematic representation of the possible structure of $H_2Ln_2Ti_3O_{10}$ is shown in Figure 2c.

A rough estimate of the interlayer separation in $H_2Ln_2Ti_3O_{10}$ can be made as follows: In $Sr_{n+1}Ti_nO_{3n+1}$, the *n* and *n* + 1 members differ in layer thickness by ~2 × 3.87 Å. Assuming that the dimensions of $[Sr_2Ti_3O_{10}]$ and $[La_2Ti_3O_{10}]$ are similar, the thickness of $[La_2Ti_3O_{10}]$ would be ~11.6 Å. This would give a value of ~1.6 Å (26.6/2 – 11.6 Å) for the interlayer distance in $H_2Ln_2Ti_3O_{10}$. This value is much smaller than the corresponding value in $HCa_2Nb_3O_{10}$.[5] The smaller value is likely to be due to the difference in stacking: in $HCa_2Nb_3O_{10}$, the perovskite slabs are stacked exactly one over the other while, in $H_2Ln_2Ti_3O_{10}$, adjacent slabs are displaced with respect to one another by $(a + b)/2$ (Figure 2c). The protons attached to the terminal oxygens in $H_2Ln_2Ti_3O_{10}$ could form hydrogen bonds in more than one way inside the semicuboctahedral cavity.

We anticipated that $H_2Ln_2Ti_3O_{10}$ would undergo dehydration at relatively low temperatures to yield perovskite oxides according to the reaction $H_2Ln_2Ti_3O_{10} \rightarrow 3Ln_{2/3}TiO_3 + H_2O$. Thermogravimetry showed that $H_2Ln_2Ti_3O_{10}$ indeed undergo dehydration around 400 °C according to this reaction. The dehydrated product in the case of lanthanum crystallizes around 1000 °C to give a single-phase product; the X-ray pattern could be indexed in a perovskite-like tetragonal cell with $a = 3.893$, $c = 7.789$ Å. Similar defective perovskites, $La_{2/3}TiO_{3-x}$ ($x = 0.007$–0.079), have been prepared earlier by Abe and Uchino.[12] In the temperature region

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(8) Dion, M.; Ganne, M.; Tournoux, M. Ravez, J. *Rev. Chim. Miner.* **1984**, *21*, 92.

(9) $Na_2La_2Ti_3O_{10}$, for example, was prepared by treating 1 g of $K_2La_2Ti_3O_{10}$ with 10 g of molten $NaNO_3$ at 300 °C for 2 days; $NaNO_3$ was replaced once in between. The solid product was washed with water and air-dried. The exchange was found to be complete by flame photometry. $Na_2La_2Ti_3O_{10}$ is tetragonal ($a = 3.834$ (7), $c = 28.65$ (6) Å). We could not prepare a hydrated analogue of $Na_2La_2Ti_3O_{10}$. Exchange of potassium in $K_2La_2Ti_3O_{10}$ by lithium using molten $LiNO_3$ required longer periods (2 weeks).

(10) $H_2Ln_2Ti_3O_{10}$ was prepared by treating 1-g samples of $K_2Ln_2Ti_3O_{10}{\cdot}H_2O$ with 100 cm^3 of 2 M HNO_3 at 30 °C for 5 days with replacement of acid every day. The exchange was found to be complete by determination of potassium in the filtrate using flame photometry. Treatment of $K_2La_2Ti_3O_{10}$ with 2 M HNO_3 at 60 °C resulted in collapse of the structure, leaving behind TiO_2.

(11) It is significant that although barium analogues of $K_2Ln_2Ti_3O_{10}$ could be prepared, it is not possible to exchange barium with protons under similar conditions. For example, $BaLa_2Ti_3O_{10}$ on treatment with dilute HNO_3 hydrolyzes to give TiO_2. However, $Na_2La_2Ti_3O_{10}$ can be prepared by treating $BaLa_2Ti_3O_{10}$ with molten NaCl.

(12) Abe, M.; Uchino, K. *Mater. Res. Bull.* **1974**, *9*, 147.

500–900 °C, $La_{2/3}TiO_3$ has a c of ~12 Å, which is probably due to its presence as a three-layered perovskite with one layer of vacant B sites for each two layers of occupied B sites. The dehydrated products for Ln = Sm, Gd, and Dy also retain the layer-like features. On heating at 950 °C, however, they transformed to $Ln_2Ti_2O_7$ pyrochlores rather than to the perovskites.

In summary, we have synthesized a new series of layered perovskites of the formula $A_2Ln_2Ti_3O_{10}$ for various rare earths and lanthanum and shown that the interlayer alkali-metal ions can be exchanged with protons as well as other alkali-metal ions under mild conditions. We are investigating Brønsted acidity and intercalation chemistry of $H_2Ln_2Ti_3O_{10}$.

At the end of this work we became aware of a recent paper on crystal chemistry and ion-exchange reactions of $Na_2Gd_2Ti_3O_{10}$.[13]

Acknowledgment. We thank Professor C. N. R. Rao, FRS, for valuable advice and encouragement. Our thanks are also due to Dr. A. J. Jacobson of Exxon Research and Engineering Co. for helpful suggestions. The Department of Sciences and Technology, Government of India, and the University Grants Commission, New Delhi, are thanked for support of this research.

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Received July 16, 1987

Monomeric versus Dimeric Vanadium(III) Aryloxide Formation. Syntheses and Crystal Structures of $[(O\text{-}2,6\text{-}ArMe_2)_2(\mu\text{-}O\text{-}2,6\text{-}ArMe_2)V^{III}]_2\cdot thf$ and $[(O\text{-}2,6\text{-}ArMe_2)_3V^{III}(py)_2]_2$ (O-2,6-ArMe$_2$ = 2,6-Dimethylphenoxide)

Sir:

Interest in the chemistry of low- and medium-valent transition-metal alkoxides has been steadily increasing in recent years.[1,2] Curiously, the group VB (group 5[17]) di- and trivalent metal alkoxides are almost unknown although an attractive reactivity has been shown in a few reported cases.[3-5]

These considerations prompted us to attempt the synthesis of low-valent vanadium aryloxides. In spite of the well-known ability of V(II) to disproportionate,[5] we have used the V(II) compounds $[[V(dmb)_2]_2\cdot(thf)]^2$ (dmb = dimethoxyphenyl)[6] (**1**) and $VCl_2(py)_4$ (**2**)[7] as starting reagents to gain some insights on the stability of complexes in this elusive oxidation state.

The room temperature reaction of **1** with 2,6-dimethylphenol in toluene, affords the unprecedented dinuclear V(III) tris(aryloxide) $[[(\mu\text{-}O\text{-}2,6\text{-}ArMe_2)(O\text{-}2,6\text{-}ArMe_2)_2V]_2(thf)]\cdot C_7H_8$ (**3**)[8] (Scheme I). A single-crystal X-ray analysis[9] of **3** showed the molecule as a dimer containing the vanadium atoms in two different coordination environments (Figure 1). In fact, surprisingly, only one of the two interstitial thf molecules of the starting material remains coordinated to one of the two metallic centers. The geometry around V2 can be described as a slightly distorted trigonal bipyramid [O4–V2–O7 = 167.0 (1)°] in which the axial positions are occupied by the thf molecule and one bridging aryloxide group with the V2 atom lying in the O1–O2–O3 plane [distance from the plane 0.066 (1) Å]. The V1–O4–V2–O1 backbone is planar [dihedral angle 0.1 (3)°]. The coordination

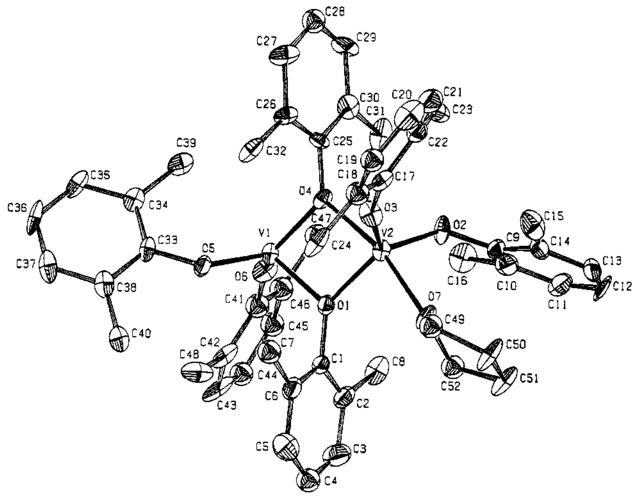

Figure 1. ORTEP drawing of **3**. Selected interatomic distances (Å) and angles (deg) (estimated standard deviations in parentheses): V1–V2 = 3.113 (1), V1–O1 = 1.999 (4), V2–O1 = 1.972 (3), V2–O4 = 2.084 (4), V1–O4 = 1.926 (3), V2–O7 = 2.119 (4), V2–O2 = 1.836 (4), V2–O3 = 1.842 (4), V1–O6 = 1.818 (4), V1–O5 = 1.831 (3), V1–C39 = 3.043 (6), O5–C33 = 1.363 (6), O2–C9 = 1.378 (6), O3–C17 = 1.346 (7), O6–C41 = 1.365 (7); V1–O4–V2 = 101.8 (2), V1–O1–V2 = 103.2 (2), O1v1–O4 = 79.0 (1), O1–V2–O4 = 76.0 (1), O2–V2–O4 = 95.0 (2), O2–V2–O7 = 94.2 (2), O1–V2–O$_2$ = 117.0 (2), O1–V2–O7 = 91.7 (1), O1–V2–O3 = 123.1 (2), O2–V2–O3 = 119.5 (2), O3–V2–O4 = 93.1 (2), O2–V2–O4 = 95.0 (2), O4–V2–O7 = 167.0 (1), O3–V2–O7 = 90.3 (2), O4–V1–O5 = 117.5 (2), O5–V1–O6 = 113.5 (2), O1–V1–O5 = 103.5 (2), O1–V1–O6 = 112.1 (2), O4–V1–O6 = 123.0 (2), V2–O2–C9 = 139.6 (4), V2–O3–C17 = 158.3 (3), V1–O6–C41 = 154.1 (4), V1–O5–C33 = 134.6 (4), C33–C38–C40 = 121.0 (5), C33–C34–C39 = 121.1 (5), V1–O5–C33–C34 = 25.7 (1), V2–O2–C9–C14 = 66.4 (1).

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(6) Cotton, F. A.; Lewis, G. E.; Mott, G. N. *Inorg. Chem.* **1983**, *22*, 560.

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(8) In a standard experiment, a solution of $[V(dmb)_2thf]_2$ (2.00 g, 2.5 mmol) in toluene (100 mL), was reacted with neat 2,6-dimethylphenol (1.8 g, 15.0 mmol). The color changed almost instantaneously to a deep emerald green. After evaporation to dryness, the residual oil was dissolved in 50 mL of *n*-hexane. After the mixture was filtered and allowed to stand for 2 days at room temperature, deep green crystals of $[[(\mu\text{-}O\text{-}2,6\text{-}ArMe_2)(O\text{-}2,6\text{-}ArMe_2)_2V]_2(thf)]\cdot C_7H_8$ separated (0.4 g, 0.4 mmol). Another crop of crystals can be obtained by on cooling the mother liquor. Anal. Calcd (found after toluene removal in vacuo) for $C_{52}H_{62}O_7V_2$: C, 69.33 (69.25); H, 6.88 (6.92); V, 11.38 (11.40). EI-MS: no parent peak observed for $[^{12}C_{52}{}^{1}H_{62}{}^{16}O_7{}^{51}V_2]$; m/e 535 [V-(OR)$_4$], 414 [V(OR)$_3$], 293 [V(OR)$_2$]. IR [KBr, Nujol mull, ν in cm^{-1}, under N$_2$]: 2730 (vw), 1591 (7), 1470 (s), 1420 (s), 1270 (s), 1218 (vs), 1091 (s), 880 (s), 852 (s), 790 (m), 767 (s), 760 (s), 742 (m), 723 (s), 695 (m), 589 (m), 540 (m), 510 (m).

(9) X-ray diffraction data for **3**: crystal size, 0.40 × 0.30 × 0.30 mm; deep green prisms; space group $P\bar{1}$ with a = 10.797 (4) Å, b = 12.032 (3) Å, c = 19.697 (6) Å, α = 72.29 (2)°, β = 81.98 (0)°, γ = 86.35 (2)°, V = 2413.1 (4) Å^3, Z = 2, and d_{calcd} = 1.369 g/cm^3, μ(Mo) = 4.28 cm^{-1}; $F(000)$ = 1056; data were collected on an Enraf-Nonius CAD-4F diffractometer; Mo radiation λ = 0.71073 Å, scan mode = $\theta/2\theta$, scan width = 0.90°; T = −130, °C; measured reflection range hkl = $+h,\pm k,\pm l$; $(\sin\theta)/\lambda$ limit (Å^{-1}) = 0.57 ($2\theta_{max}$ = 48°); number of unique reflections, 6805; number of reflections used in analysis, 5177 [$I > 3\sigma(I)$]; structure solved by direct methods; all non-hydrogen atom positions were located and refined anisotropically including an extremely disordered molecule of toluene (isotropically refined); all hydrogen atom positions were located from difference Fourier maps, but isotropic refinement was not possible for the methyl hydrogen atoms except those bonded to C31, C47, and C48; number of variables, 787; R = 0.056; R_w = 0.067, $w = 1/\sigma^2(F_o)$; GOF = 1.78; largest remaining peak, 1.23 e/Å^3; largest shift/esd, final cycle, 0.03.

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