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Preliminary communication

Synthesis and structure of heterometallic cluster complexes. Reaction of imido complex $LWRu_2(CO)_8(\mu\text{-}H)(\mu_3\text{-}NPh)$, L = Cp and Cp*, with the tungsten acetylide complex $CpW(CO)_3C{\equiv}CPh$

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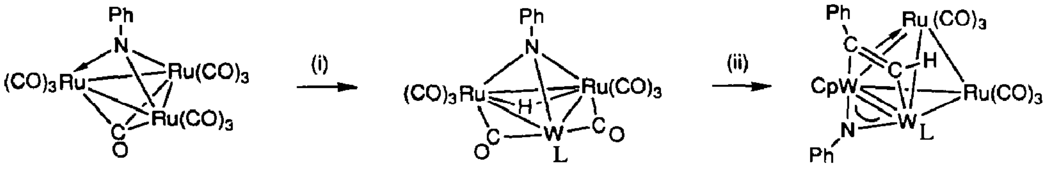
Abstract

The triruthenium imido cluster $Ru_3(CO)_{10}(\mu_3\text{-}NPh)$ reacts with tungsten hydrides $LW(CO)_3H$ to give heterometallic imido clusters $LWRu_2(CO)_8(\mu\text{-}H)(\mu_3\text{-}NPh)$ (**2**, L = Cp; **3**, L = Cp*) via the process of metal–metal exchange. Treatment of the imido clusters **2** and **3** with tungsten acetylide $CpW(CO)_3C{\equiv}CPh$ produces a novel tetranuclear imidoalkyne complex $LCpW_2Ru_2(CO)_6(\mu\text{-}NPh)(\mu\text{-}\eta^2\text{-}CH{=}CPh)$ (**4**, L = Cp; **5**, L = Cp*). The structures of **2** and **5** have been characterized by single-crystal X-ray diffraction. Crystal data for **2**: space group *Cc*, *a* 18.177(5), *b* 8.672(2), *c* 16.181(5) Å, $\beta = 123.25(2)°$, $Z = 4$; $R_F = 0.0492$, $R_W = 0.0513$. Crystal data for **5**: space group $P\bar{1}$, *a* 10.130(2), *b* 11.438(1), *c* 15.423(2) Å, $\alpha = 95.99(1)$, $\beta = 92.27(1)$, $\gamma = 106.05(1)°$, $Z = 2$; $R_F = 0.026$, $R_W = 0.026$.

The chemistry of mixed-metal cluster complexes has been the subject of intensive research for many years [1]. The reason is that the structures, bonding and reactivity patterns of heterometallic clusters may differ greatly from those of the homometallic clusters. By means of the concept of isolobal analogy developed by Hoffmann [2], Stone and coworkers have used alkylidyne complexes $Cp(CO)_2W{\equiv}CR$ as a basic building block to prepare many heterometallic clusters of different nuclearities [3]. Recently, we have applied a similar strategy of using metal hydride complexes $LW(CO)_3H$ (L = Cp, Cp*) [4] and metal acetylide complexes $LW(CO)_3C{\equiv}CR$ [5] to prepare several tri- and tetranuclear heterometallic cluster complexes. In order to extend further the idea of using mononuclear metal hydride and acetylide as building blocks to prepare clusters of higher nuclearities, we have reacted the imido complexes $Ru_3(CO)_{10}(\mu_3\text{-}NPh)$ with first $LW(CO)_3H$ and then $CpW(CO)_3C{\equiv}CPh$



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L = Cp, 2; L = Cp*, 3

L = Cp, 4; L = Cp*, 5

(i) LW(CO)$_3$H, L = Cp, Cp*; (ii) CpW(CO)$_3$C≡CPh

Scheme 1.

in an attempt to prepare the heterometallic imido complexes. Furthermore, we also wish to examine the bonding mode and chemical transformation of the imido ligand on the coordination sphere of polynuclear cluster complexes.

In this report, we describe the structural studies of two novel imido complexes prepared by the specified reactions.

Treatment of the triruthenium imido complex $Ru_3(CO)_{10}(\mu_3\text{-NPh})$ (**1**) [6] with metal hydride complex LW(CO)$_3$H in refluxing toluene (110 ° C, 20 min) produced a novel trinuclear heterometallic imido cluster, $LWRu_2(CO)_8(\mu\text{-H})(\mu_3\text{-NPh})$ (**2**, L = Cp, 56%; **3**, L = Cp*, 51%) in addition to trace properties of $Ru_3(CO)_{12}$ (Scheme 1). The overall process is best understood as a metal-exchange reaction [7], in which the imido clusters **2** and **3** are produced by the replacement of the Ru(CO)$_3$ unit by an isoelectronic LW(CO)$_2$H fragment; the coproduct $Ru_3(CO)_{12}$ is generated by the trimerization of the departing Ru(CO)$_3$ unit. In conformity with the metal-exchange reaction, Geoffroy and coworkers have also reported the preparation of the heteronuclear cluster $HCoRu_2(CO)_9(\mu_3\text{-NPh})$ via addition of $[Co(CO)_4]^-$ to **1**, followed by acidification [8].

These imido complexes were separated and purified on silica gel TLC plates, and were characterized by spectroscopic methods [9*]. The ^{1}H-NMR spectra of **2** and **3** each show a sharp hydride signal at δ −16.77 and at δ −16.44, respectively, indicating that the bridging hydride is associated with the Ru–Ru bond. Solution infrared spectra of these complexes exhibit, in addition to the absorptions assigned to terminal CO ligands, a weak absorption at 1820 cm^{-1} and 1796 cm^{-1} for **2** and **3**, respectively, suggesting the presence of a semibridging CO interaction. The ^{13}C-NMR spectrum of **2** at 205 K showed one W–CO signal at δ 209.4 (J(W–C) = 179 Hz) and three Ru–CO signals at δ 196.0, 168.9 (J(C–H) = 16 Hz) and 185.1 with an intensity ratio 2:2:2:2, indicating C_s point group symmetry for these molecules. By the characteristic J(C–H) coupling, the signal at δ 168.9 is assigned to the CO ligands *trans* to the bridging hydride.

Orange-red, air-stable, crystals of **2** suitable for structural determination were obtained from a layered solution of CH_2Cl_2/CH_3OH, and a single-crystal diffraction study was performed [10*]. The molecular structure is presented in Fig. 1, which also provides selected data of bond lengths and angles. The molecule consists

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* Reference number with asterisk indicates a note in the list of references.

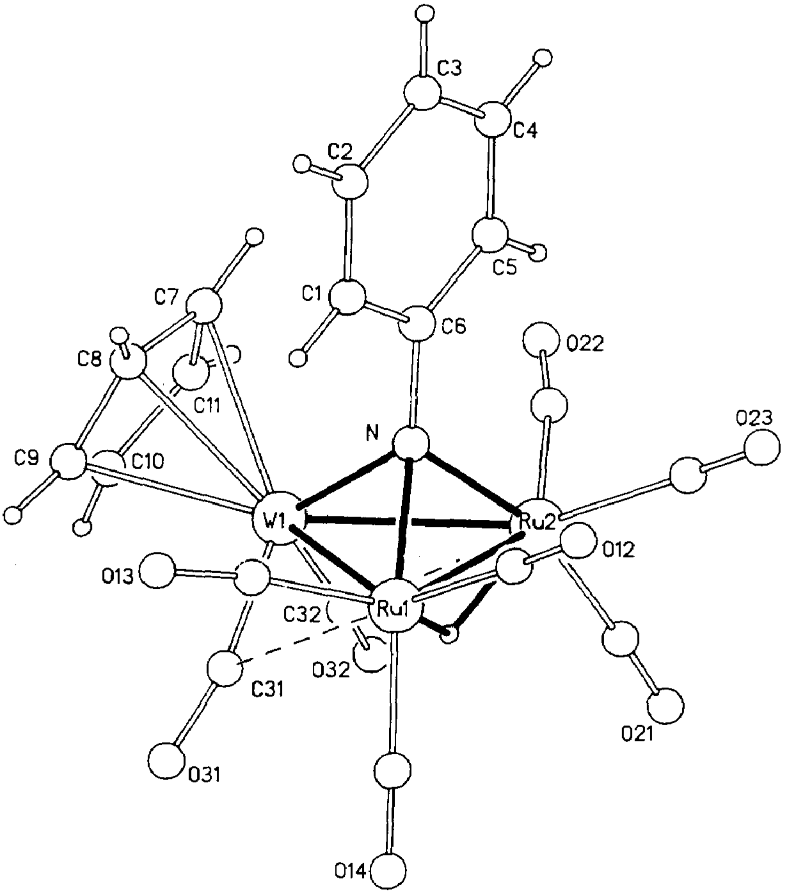

Fig. 1. Molecular structure of $CpWRu_2(CO)_8(\mu\text{-}H)(\mu_3\text{-}NPh)$ (2) showing the atomic numbering scheme. Important dimensions include: bond lengths (Å) W(1)–Ru(1) 2.810(2), W(1)–Ru(2), 2.788(2), Ru(1)–Ru(2) 2.845(3), W(1)–N 2.11(2), Ru(1)–N 2.06(3), Ru(2)–N 2.05(2), N–C(6) 1.46(2), W(1)–C(31), 1.89(2), W(1)–C(32) 1.76(3), Ru(1)–C(31) 2.59(2), Ru(2)–C(32) 2.64(2); bond angles (°) Ru(2)–Ru(1)–C(14) 118.3(9), Ru(1)–Ru(2)–C(21) 122.4(6), W(1)–C(31)–O(31) 164(2), W(1)–C(32)–O(32) 163(2).

of an isosceles WRu_2 geometry with typical bond distances W(1)–Ru(1) = 2.810(2) Å, W(1)–Ru(2) = 2.788(2) Å, and Ru(1)–Ru(2) = 2.845(3) Å. Each ruthenium atom is associated with three terminal CO ligands while the tungsten atom is capped by a Cp ligand and linked to two semi-bridging CO ligands. The imido ligand (NPh) of this molecule is located on the WRu_2 triangular face opposite the semibridging W–CO ligands and its phenyl substituent is parallel to the Ru–Ru bond presumably so as to reduce the steric interaction with the adjacent Cp ligand. The W–N distance (2.12(2) Å) and the Ru–N distances (2.05(2) Å and 2.06(3) Å) are consistent with those of the metal–nitrogen single bond. In comparison, the length of the W–N double bond of the W = N(Ph) → Ru fragment in the imido cluster $CpWRu_3(CO)_9(\mu\text{-}NPh)(C{\equiv}CPh)$ is 1.83(1) Å [5c]; the average Ru–N distances in the triruthenium clusters **1**, $Ru_3(CO)_8(DPPM)(\mu_3\text{-}NPh)$, and $H_2Ru_3(CO)_9(\mu_3\text{-}NPh)$ are in the range 2.06–2.07 Å [11]. Finally, the location of the hydride, as determined by Fourier method, is found to be associated with the unique Ru–Ru bond.

Reactions with dihydrogen, nitrosobenzene and CpW(CO)$_3$C≡CPh have been carried out in an attempt to compare its reactivity with that of the triruthenium analogue **1**. In contrast to the reactions of **1**, which produced $H_2Ru_3(CO)_9(\mu_3\text{-NPh})$ [11c] and $Ru_3(CO)_9(\mu_3\text{-NPh})_2$ [11a], respectively, treatment of imido cluster **2** with nitrosobenzene in toluene (60 °C, 5 min) and the reaction with dihydrogen in refluxing toluene (1 atm, 3 h) result only in decomposition.

However, the reaction with CpW(CO)$_3$C≡CPh is successful. Treatment of both **2** and **3** with 1 : 1.2 molar ratio of CpW(CO)$_3$C≡CPh in toluene (110 °C, 40 min) generates a condensation product $LCpW_2Ru_2(CO)_6(\mu\text{-NPh})(\mu\text{-}\eta^2\text{-CH=CPh})$ (**4**, L = Cp, 38%; **5**, L = Cp*, 35%) in moderate yield (Scheme 1). Complexes **4** and **5** were initially characterized by microanalysis and spectroscopic methods [12*]. ^{1}H-NMR studies suggest that the incoming acetylide fragment has inserted into the Ru–H–Ru bond of the bridging hydride. Variable-temperature ^{13}C-NMR spectra of complex **5** (CD_2Cl_2) indicate that the molecule possesses two $Ru(CO)_3$ fragments undergoing rapid, localized, three-fold rotation in solution. The ^{13}C-NMR spectrum at 196 K shows three CO signals of equal intensity at δ 216.9, 213.8, and 195.6 and three broad CO signals of equal intensity at δ 210.7, 209.5 and 198.4. When the solution was warmed to 294 K, the first three CO signals coalesce to give a relatively broad CO signal at δ 207.5 and the second set of three CO signals forms a sharp CO signal at δ 205.9.

We have studied compound **5** by X-ray diffraction to establish its structure [13*]. The molecular structure and the scheme used for labeling the atoms are illustrated in Fig. 2. In this molecule, the tungsten atoms and ruthenium atoms form a distorted tetrahedral core arrangement, in which each Ru atom is associated with three terminal CO ligands and the tungsten atoms W(1) and W(2) are capped by Cp and Cp* ligands, respectively. The alkyne ligand, which is derived from the acetylide fragment, is here coordinated to both tungsten atoms via a σ-bond and to the Ru(1) atom via a π-bond; this bonding mode is similar to the typical μ_3-η^2-($\|$) interaction in alkyne trimetal clusters [14]. The imido group is coordinated symmetrically to the W(1)–W(2) edge with the W–N distances (1.932(5) and 1.937(5) Å) in the range between those of the W–N single bond (2.12(2) Å) observed in **2** and the W–N double bond (1.83(1) Å) of $CpWRu_3(CO)_9(\mu\text{-NPh})$(C≡CPh) [5c]. Therefore, multiple-bond character is evidently present.

In addition, simple count of formal electrons suggests that this tetrahedral cluster is associated with only 58 valence electrons, and as such is unsaturated. In accordance with this property the W(1)–W(2) distance (2.592(1) Å) is much shorter than other metal–metal bonds in the molecule (2.926(1)–2.736(1) Å), presumably reflecting the existence of some multiple-bond character. Consistent with this attribute, the distance of the W(1)–W(2) bond is within the range of W–W double bonds of several W_2 dinuclear complexes [15]. Furthermore, the observed bonding mode of the local $\overline{W(\mu\text{-NPh})W}$ arrangement resembles that of the local $\overline{W(\mu\text{-CR})W}$ arrangement of the unsaturated trinuclear complexes $Cp_2W_2Os(CO)_5(\mu\text{-CTol})(\mu_3\text{-CTol})$ [16] and $Cp_2W_2Re(CO)_3(\mu\text{-Br})(\mu\text{-X})(\mu\text{-CTol})(\mu_3\text{-CTol})$ (X = O and CO) [17] for which the W_2C triangular arrangement involving tungsten–tungsten and tungsten–carbon multiple bonding has been invoked.

In summary, this work has introduced a convenient method to prepare trinuclear heterometallic clusters $LWRu_2(CO)_8(\mu\text{-H})(\mu_3\text{-NPh})$ containing a triply bridging imido ligand. Further reaction with CpW(CO)$_3$C≡CPh generates a tetranuclear

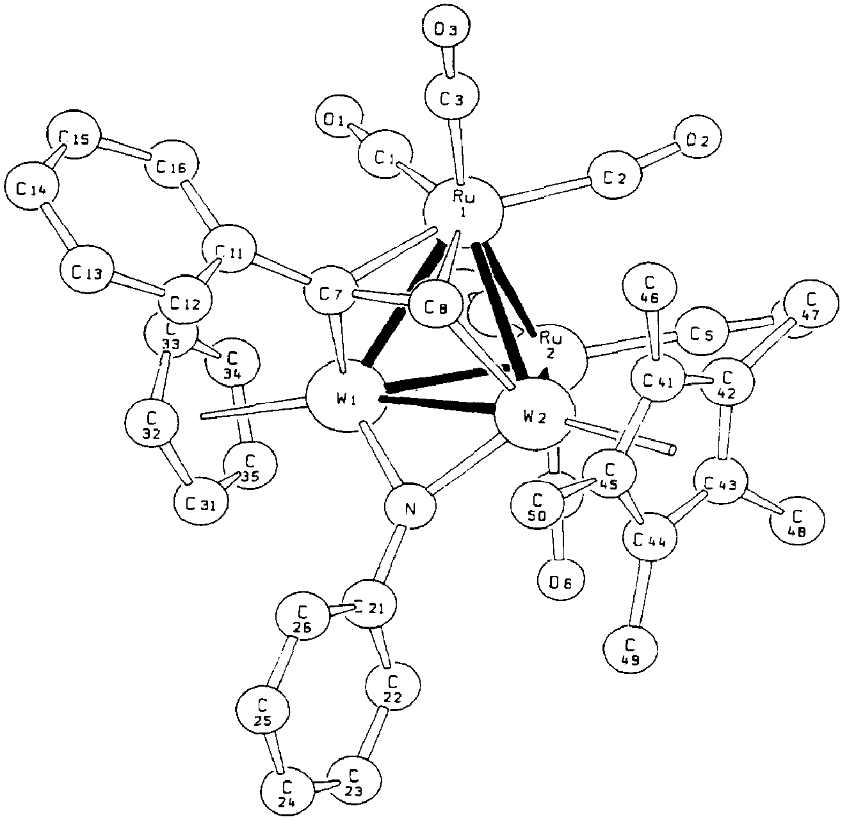

Fig. 2. Molecular structure of $Cp^{\star}CpW_2Ru_2(CO)_6(\mu\text{-}\eta^2\text{-}CH{=}CPh)(\mu\text{-}NPh)$ (**5**) showing the atomic numbering scheme. Important dimensions include: bond lengths (Å) W(1)–W(2) 2.592(1), W(1)–Ru(1) 2.829(1), W(1)–Ru(2) 2.744(1), W(2)–Ru(1) 2.926(1), W(2)–Ru(2) 2.736(1), W(1)–N 1.932(5), W(2)–N, 1.937(5), W(1)–C(7) 2.095(6), W(2)–C(8) 2.057(6), Ru(1)–C(7) 2.178(6), Ru(1)–C(8) 2.188(6); bond angle W(1)–N–W(2) 84.1(2)°.

cluster complex $LCpW_2Ru_2(CO)_6(\mu\text{-}NPh)(\mu\text{-}\eta^2\text{-}CH{=}CPh)$, in which the imido ligand has migrated from the WRu_2 triangle to the W–W edge to give a highly unsaturated $\overline{W(\mu\text{-}NPh)W}$ core arrangement. Furthermore, from the relative locations of the phenyl substituent of the alkyne ligand and the CpW fragment in complex **5**, we propose that the tungsten atom of the incoming metal acetylide has also undergone a 1,2-shift from the α-carbon to the β-carbon during the condensation. Migration of an isoelectronic $CpFe(CO)_2$ fragment in $CpFe(CO)_2C{\equiv}CPh$ has been reported recently [18], in which the addition of an organometallic electrophile $[Re(CO)_5]^+$ induces the change of the bonding mode of the $CpFe(CO)_2$ fragment from σ-bond to π-bond. The π-complex isolated can be considered as an intermediate for the 1,2-shift observed in our system.

Note added in proof. After submission of this paper, an article which deals the reversible interconversion of $CpFe(CO)_2$ fragments from σ- to π-bonding in the system of dinuclear Fe_2 acetylide complexes appeared [19].

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9 Selected spectral data for 2: MS (FAB, ^{102}Ru, ^{184}W): m/z 769 (M^+); IR(C_6H_{12}): ν(CO) 2089 (s), 2069 (vs), 2024 (vs), 2007 (m), 1870 (w), 1820 (vw) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 294 K): δ 7.17–6.90 (m, 5H), 5.22 (s, 5H), −16.77 (s, 1H); ^{13}C NMR (100.4 MHz, CD_2Cl_2, 205 K): δ 209.4 (J(W–C) = 179 Hz, W–CO), 196.0 (Ru–CO), 1689 (J(C–H) = 16 Hz, Ru–CO), 185.1 (Ru–CO). Elemental analysis: Found: C, 29.68; H, 1.48; N, 1.84. $W_1Ru_2C_{19}H_{11}N_1O_8$ calcd.: C, 29.74; H, 1.45; N, 1.83%. Selected spectral data for 3: MS (FAB, ^{102}Ru, ^{184}W): m/z 839 (M^+); IR (C_6H_{12}): ν(CO) 2086 (s), 2067 (vs), 2023 (vs), 1998 (br,m), 1846 (w), 1796 (vw) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 294 K): δ 7.14–6.97 (m, 5H), 1.76 (s, 15H), −16.44 (s, 1H). Elemental analysis: Found: C, 34.30; H, 2.55; N, 1.68. $W_1Ru_2C_{24}H_{21}N_1O_8$ calcd.: C, 34.42; H, 2.53; N, 1.67%.

10 Crystal data for 2: $W_1Ru_2C_{19}H_{11}N_1O_8$, M = 767.29, monoclinic, space group Cc, a 18.177(5), b 8.672(2), c 16.181(5) Å, β = 123.25(2)°, V 2132.93 Å^3, Z = 4, D_c 2.389 g/cm^3, $F(000)$ = 1432, Mo-K_α radiation with λ = 0.71073Å, 2403 unique reflections were measured of which 2375 were considered observed with $I > 3\sigma(I)$. The structure was solved using the SHELXTL PLUS software package and refined by full matrix least-squares recycle. Final R = 0.0492, R_w = 0.0513, GOF = 6.0479. Details of the structure data may be obtained from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2 (F.R.G.), on quoting the depository number CSD-53874, the names of the authors, and the journal citation.

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12 Selected spectral data for 4: MS (FAB, ^{102}Ru, ^{184}W): m/z 1163 (M^+); IR(C_6H_{12}): ν(CO) 2034 (s), 2003 (vs), 1972 (m), 1966 (br,w), 1926 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 294 K): δ 9.57 (s, 1H), 7.25–7.20 (m, 4H), 7.05 (q, 2H), 6.83 (d, 2H), 6.40 (d, 2H), 5.81 (s, 5H), 5.53 (s, 5H). Elemental analysis: Found: C, 33.68; H, 1.93; N, 1.35. $W_2Ru_2C_{30}H_{21}N_1O_6$ calcd.: C, 33.95; H, 1.99; N, 1.32%. Selected spectral data for 5: MS (FAB, ^{102}Ru, ^{184}W): m/z 1109 (M^+); IR(C_6H_{12}): ν(CO) 2037 (s), 2008 (vs), 1975 (m), 1965 (s), 1930 (m) cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2, 294 K): δ 9.16 (s, 1H), 7.31–7.22 (m, 4H), 7.07 (q, 2H), 6.91 (d, 2H), 6.56 (d, 1H), 6.37 (d, 1H), 5.45 (s, 5H), 1.93 (s, 15H); ^{13}C NMR (100.4 MHz, CD_2Cl_2, 186 K): M–CO, δ 216.9, 213.8, 210.7, 209.5, 198.4, 195.6; δ 167.2 (J(W–C) = 89 Hz, CPh = CH), 151.6 (J(W–C) = 99 Hz, J(C–H) = 159 Hz, CPh = CH). Elemental analysis: Found: C, 37.05; H, 2.72; N, 1.29. $W_2Ru_2C_{35}H_{31}N_1O_6$ calcd.: C, 37.15; H, 2.76; N, 1.24%.

13 Crystal data for 5: $W_2Ru_2C_{35}H_{31}N_1O_6$, M = 1131.46, triclinic, space group $P\bar{1}$, a 10.130(2), b 11.438(1), c 15.423(2) Å, α = 95.99(1), β = 92.27(1), γ = 106.05(1)°, V 1703.58 Å^3, Z = 2, D_c 2.206 g/cm^3, $F(000)$ = 1063.71, Mo-K_α radiation with λ = 0.71073Å, 5988 unique reflections were measured of which 5104 were considered observed with $I > 2.5\sigma(I)$. The structure was solved and refined

by using the NRCC-SPD-VAX packages. Final $R = 0.026$, $R_w = 0.026$, GOF = 2.371. Tables of bond distances and angles, tables of positional parameters and anisotropic thermal parameters, and listings of the observed and calculated structural factors are available from the author (L.-K. L).

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