# Preparation of Some Oxoniobium Carboxylates. X-Ray Crystal and Molecular Structure of [{$NbCl_3(O_2CPh)$}$_2$O]*

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Reaction of $NbCl_5$ with aryl carboxylic acids yields the oxoniobium carboxylates [{$NbCl_3(O_2CR)$}$_2$O] (R = Ph, *p*-$MeC_6H_4$, *o*-$MeC_6H_4$, *p*-$FC_6H_4$, *p*-$ClC_6H_4$, *o*-$FC_6H_4$, *o*-$ClC_6H_4$, *o*-$BrC_6H_4$ or 2,6-$Cl_2C_6H_3$). Crystal structure analysis of the benzoate derivative shows the presence of a μ-oxo-bis(μ-carboxylato) dimetal core; each niobium atom is in a distorted octahedral environment, the other three sites on each metal being occupied by chlorine atoms. Spectroscopic data suggest similar structures for the remaining species.

While the chemistry of metal carboxylates, and their associated oxo species, is reasonably well documented,[1,2] the only fully characterised carboxylate derivatives containing niobium(v) are the oxalato complexes $[NH_4]_3[NbO(C_2O_4)_3]\cdot H_2O$ and $[NH_4]_3[Nb(O_2)_2(C_2O_4)_2]\cdot H_2O$ whose structures have been determined from X-ray data.[3] We have undertaken a study of niobium(v) carboxylate species and report here the preparation and properties of a series of derivatives including the first example of a niobium(v) compound with a μ-oxo-bis(μ-carboxylato) dimetal core. Compounds containing the [M(μ-O)(μ-$O_2CR)_2$M] unit have been previously reported for other early transition metals, namely Ti, V, Cr, Mn[4,5,6] and Fe$^{III}$[7] as exemplified by the complexes [{Fe(μ-$O_2$CMe)[HB(pz)$_3$]}$_2$O] and [{Fe(μ-$O_2$CMe)(tacn)}$_2$O]$I_2$ [HB(pz)$_3$ = hydrotris(pyrazol-1-yl)borate, tacn = 1,4,7-triazacyclononane].[8,9]

## Results and Discussion

Reaction of $NbCl_5$ with an aryl carboxylic acid in a 1 : 1.5 molar ratio in chloroform or carbon tetrachloride affords, after heating to 60–110 °C, the oxo complexes [{$NbCl_3(O_2CR)$}$_2$O] (R = Ph, *p*-$MeC_6H_4$, *o*-$MeC_6H_4$, *p*-$FC_6H_4$, *p*-$ClC_6H_4$, *o*-$FC_6H_4$, *o*-$ClC_6H_4$, *o*-$BrC_6H_4$ or 2,6-$Cl_2C_6H_3$) as yellow or yellow-orange powders in good yield. The reactions proceed as shown in equation (1). The oxo ligand is provided by the organic acid with the corresponding acid chloride (identified by IR spectroscopy in the reaction liquor) being produced as a by-product. Abstraction of an oxygen atom from a carboxylic acid by an early transition metal chloride has been noted previously. Thus a metal–oxo group is reported to occur in the preparation of $[NbOCl_2(O_2CR)]$ (R = alkyl) species[10] [equation (2)], whilst we have reported other related reactions [equations (3) and (4)] involving the use of titanium tetrachloride.[11,12]

$$2\,NbCl_5 + 3\,RCO_2H \longrightarrow [\{NbCl_3(O_2CR)\}_2O] + RCOCl + 3\,HCl \quad (1)$$

$$2\,NbCl_5 + 4\,RCO_2H \longrightarrow 2\,[NbOCl_2(O_2CR)] + 2\,RCOCl + 4\,HCl \quad (2)$$

$$3\,TiCl_4 + 7\,RCO_2H \longrightarrow [Ti_3Cl_3(O_2CR)_5O_2] + 2\,RCOCl + 7\,HCl \quad (3)$$

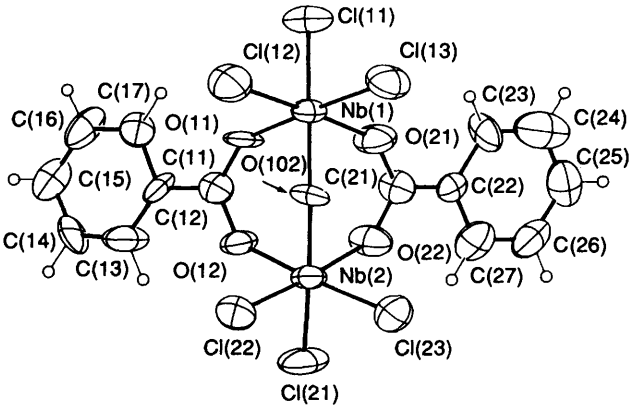

Fig. 1 Molecular structure of [{$NbCl_3(O_2CPh)$}$_2$O] with atom labelling

$$4\,TiCl_4 + 8\,PhCO_2H \longrightarrow [Ti_4Cl_6(O_2CPh)_6O_2] + 2\,PhCOCl + 8\,HCl \quad (4)$$

When $NbCl_5$ and benzoic acid were reacted at room temperature in a 1 : 1 molar ratio the IR spectrum of the yellow solid obtained indicated that it was a mixture of products including a small amount of [{$NbCl_3(O_2CPh)$}$_2$O] which was isolated by recrystallisation. It has not yet proved possible to identify the other constituents of the mixture, and it is relevant to note that this reaction appears to follow a different pathway from that involving alkyl acids where similar reaction conditions have been reported to yield only the chloro carboxylate $[NbCl_4(O_2CR)]$ (R = alkyl).[13]

*Structural Study*.—The structure of [{$NbCl_3(O_2CPh)$}$_2$O] as determined by X-ray crystallography is shown in Fig. 1. Selected bond lengths and angles are given in Table 1 and the atomic coordinates in Table 2. The complex has a characteristic dinuclear structure, similar to that observed in some titanium carboxylates.[6] Each niobium atom shows a slightly distorted octahedral co-ordination, and the steric limitations imposed by the bite of the bidentate bridging benzoate forces the equatorial ($O_2Cl_2$) planes around the metal atoms away from a parallel orientation. A further consequence of the steric requirement is that such structures appear to be limited in the bridging unit to *two* carboxylate groups and a *single* bridging oxygen atom. For three or four bridging carboxylates a metal–metal bond would be required as for example in $[Cu_2(O_2CMe)_4(C_5H_5N)_2]$.[14]

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

**Table 1** Selected bond lengths (Å) and angles (°) for $[\{NbCl_3(O_2CPh)\}_2O]$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Nb(1)–Cl(11) | 2.320(7) | Nb(1)–O(11) | 2.04(2) | Nb(2)–Cl(21) | 2.320(7) | Nb(2)–O(12) | 2.06(2) |
| Nb(1)–Cl(12) | 2.283(8) | Nb(1)–O(21) | 2.06(2) | Nb(2)–Cl(22) | 2.274(8) | Nb(2)–O(22) | 2.08(2) |
| Nb(1)–Cl(13) | 2.268(8) | C(11)–O(11) | 1.25(3) | Nb(2)–Cl(23) | 2.288(8) | C(21)–O(21) | 1.23(3) |
| Nb(1)–O(102) | 1.911(1) | C(11)–O(12) | 1.03(3) | Nb(2)–O(102) | 1.89(1) | C(21)–O(22) | 1.31(3) |
| | | | | | | | |
| Cl(11)–Nb(1)–Cl(12) | 96.1(3) | Cl(21)–Nb(2)–O(102) | 162.8(5) | Cl(12)–Nb(1)–Cl(13) | 94.6(3) | Cl(22)–Nb(2)–O(12) | 91.0(5) |
| Cl(11)–Nb(1)–Cl(13) | 95.7(3) | Cl(21)–Nb(2)–O(12) | 82.6(4) | Cl(12)–Nb(1)–O(102) | 95.6(5) | Cl(22)–Nb(2)–O(22) | 176.0(5) |
| Cl(11)–Nb(1)–O(102) | 162.9(4) | Cl(21)–Nb(2)–O(22) | 84.0(5) | Cl(12)–Nb(1)–O(11) | 90.3(5) | Cl(23)–Nb(2)–O(102) | 96.3(5) |
| Cl(11)–Nb(1)–O(11) | 84.1(4) | Cl(23)–Nb(2)–O(12) | 174.4(5) | Cl(12)–Nb(1)–O(21) | 175.9(5) | Cl(23)–Nb(2)–O(22) | 89.4(5) |
| Cl(11)–Nb(1)–O(21) | 84.4(5) | O(102)–Nb(2)–O(12) | 84.3(6) | Cl(13)–Nb(1)–O(102) | 95.8(5) | O(12)–Nb(2)–O(22) | 85.1(6) |
| O(102)–Nb(1)–O(11) | 83.4(6) | O(102)–Nb(2)–O(22) | 83.9(6) | Cl(13)–Nb(1)–O(11) | 175.1(5) | O(11)–Nb(1)–O(21) | 85.7(6) |
| O(102)–Nb(1)–O(21) | 83.1(6) | Nb(1)–O(102)–Nb(2) | 143.1(7) | Cl(13)–Nb(1)–O(21) | 83.1(6) | Nb(1)–O(1)–C(11) | 139(1) |
| Cl(21)–Nb(2)–Cl(22) | 96.4(3) | Nb(2)–O(12)–C(11) | 135(1) | Cl(22)–Nb(2)–Cl(23) | 94.6(3) | Nb(2)–O(22)–C(21) | 136(1) |
| Cl(21)–Nb(2)–Cl(23) | 95.8(3) | Nb(1)–O(21)–C(21) | 140(2) | Cl(22)–Nb(2)–O(102) | 94.8(5) | | |

**Table 2** Fractional atomic coordinates (× $10^4$) for $[\{NbCl_3(O_2CPh)\}_2O]$ with estimated standard deviations in parentheses

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Nb(1) | 2175.9(19) | 1679.1(14) | 4087.8(12) |
| Nb(2) | 5542.3(20) | 1615.2(15) | 5280.7(12) |
| Cl(11) | 445(7) | 2503(4) | 3479(4) |
| Cl(12) | 2328(7) | 891(5) | 2980(5) |
| Cl(13) | 677(7) | 873(4) | 4676(5) |
| Cl(21) | 7376(7) | 2375(5) | 5882(5) |
| Cl(22) | 6910(7) | 735(4) | 4685(4) |
| Cl(23) | 5309(7) | 852(4) | 6401(4) |
| O(102) | 3847(14) | 1295(8) | 4687(9) |
| O(11) | 3528(14) | 2464(9) | 3644(9) |
| O(12) | 5665(15) | 2390(9) | 4332(9) |
| C(11) | 4814(24) | 2620(13) | 3712(14) |
| C(12) | 5455(25) | 3124(13) | 3124(12) |
| C(13) | 6849(24) | 3278(16) | 3142(16) |
| C(14) | 7355(25) | 3748(15) | 2577(15) |
| C(15) | 6489(29) | 4082(13) | 1976(14) |
| C(16) | 5081(30) | 3945(15) | 1946(15) |
| C(17) | 4528(25) | 3469(16) | 2494(14) |
| O(21) | 2159(17) | 2435(10) | 5065(10) |
| O(22) | 4277(16) | 2463(9) | 5749(10) |
| C(21) | 2937(25) | 2648(13) | 5665(14) |
| C(22) | 2432(15) | 3100(7) | 6292(8) |
| C(23) | 979(15) | 3206(7) | 6263(8) |
| C(24) | 406(15) | 3616(7) | 6884(8) |
| C(25) | 1287(15) | 3920(7) | 7534(8) |
| C(26) | 2740(15) | 3813(7) | 7562(8) |
| C(27) | 3313(15) | 3403(7) | 6941(8) |
| C(001)[a] | 2912(42) | −529(24) | 1131(24) |
| C(002)[b] | 1186(79) | −356(51) | −573(52) |
| C(003)[a] | 468(42) | −778(25) | 8(26) |
| C(004)[b] | 2288(68) | −691(42) | 866(44) |
| C(005)[b] | 900(65) | 611(41) | 904(42) |
| C(006)[b] | 1898(70) | 884(41) | 459(42) |
| C(007)[b] | 3244(91) | 310(59) | −190(61) |
| C(008)[b] | 2867(94) | −484(61) | 700(62) |
| C(009)[b] | 3979(101) | −222(72) | 298(75) |
| C(010)[b] | 2262(82) | 316(52) | −451(53) |

[a] 0.5 Occupancy. [b] 0.25 Occupancy.

Within the $[M(\mu\text{-}O_2CR)_2(\mu\text{-}O)M]$ fragment the Nb–O–Nb bridge is appreciably bent, as may now be expected for $d^0$ metal complexes of this type.[6] The Nb–O–Nb angle is 143.1°, with an average Nb–O distance of 1.90 Å. These values may be compared with those for the titanium(IV) complex $[\{TiCl_2(O_2CPh)(EtO_2CMe)\}_2O]$ where the Ti–O–Ti angle is 137.2° and the Ti–(μ-O) distance is 1.78 Å.[6] This shorter Ti–O distance may be associated with the group *trans* to the bridging oxygen being the ethyl acetate ligand, whereas in the present case the *trans* group is the relatively stronger bonded chlorine. It is noteworthy that apart from this difference in bond distances the other parameters [M–Cl and M–O(carboxylate) distances] are comparable for the niobium(V) and titanium(IV) compounds, with the former being only about 0.01–0.02 Å greater.

Spectroscopic studies (IR and NMR, see Experimental section) for all the compounds are consistent with the occurrence of the structural type illustrated by $[\{NbCl_3(O_2CPh)\}_2O]$, with the IR spectra clearly indicating the presence of bridging carboxylate groups. From the similarities in the spectra of all the compounds it would appear that they all possess structures closely related to that observed for the benzoate derivative.

## Experimental

Infrared spectra (4000–200 $cm^{-1}$) were recorded from hexachlorobutadiene or Nujol mulls using CsI plates and a Perkin Elmer 580B or 1720X FT spectrophotometer. Proton NMR spectra were run on a Bruker ACF 250 (250 MHz) spectrometer in $CDCl_3$. Microanalyses were performed by Butterworths Laboratories, Teddington. The complexes are air sensitive and were prepared and handled under dry nitrogen using standard Schlenk techniques and glove boxes. All solvents were dried by distillation from $CaH_2$ prior to use. Niobium pentachloride (Aldrich) and the organic acids were used as supplied.

*Preparation of* $[\{NbCl_3(O_2CR)\}_2O]$ *Species*.—A typical procedure (for R = Ph) is as follows. Benzoic acid (2.6 g, 21.1 mmol) was added under a $N_2$ atmosphere to a magnetically stirred suspension of $NbCl_5$ (3.8 g, 14.1 mmol) in $CHCl_3$ (80 $cm^3$). The mixture was then heated to reflux for 2 h with stirring. The resulting orange-brown solution was allowed to cool, filtered and the liquor removed at the pump. A yellowish solid was produced which was stirred in hexane (50 $cm^3$) before being filtered off, washed further with hexane (2 × 50 $cm^3$) and dried *in vacuo* for 8 h. The compound was recrystallised from $CH_2Cl_2$–hexane using the layering technique. Yield 2.2 g (46%) (Found: C, 27.30; H, 1.65; Nb, 28.15. $C_{14}H_{10}Cl_6Nb_2O_5\cdot 0.25C_6H_{14}$ requires C, 27.45; H, 2.00; Nb, 27.40%). Major IR bands at 1597, 1494 [$\nu_{asym}(CO_2^-)$], 1420, 1407 [$\nu_{sym}(CO_2^-)$], 1314, 720, 370, 340 and 300 $cm^{-1}$. $^1H$ NMR, δ 7.4–8.6 (m). The NMR data indicated the presence of solvent ($C_6H_{14}$) in the compound (complex:solvent 1:0.25) which could not be removed even by prolonged pumping. Other $[\{NbCl_3(O_2CR)\}_2O]$ compounds were prepared similarly using either $CHCl_3$ (R = *p*-$FC_6H_4$, *p*-$ClC_6H_4$, *o*-$BrC_6H_4$, *o*-$MeC_6H_4$ or 2,6-$Cl_2C_6H_3$) or $CCl_4$ (R = *o*-$ClC_6H_4$, *p*-$MeC_6H_4$ or *o*-$FC_6H_4$) as solvent.

R = *p*-$FC_6H_4$. Yield 39% (Found: C, 24.15; H, 1.30. $C_{14}H_8Cl_6F_2Nb_2O_5$ requires C, 24.25; H, 1.15%). IR: 1480 [$\nu_{asym}(CO_2^-)$], 1402 [$\nu_{sym}(CO_2^-)$], 1320, 1272, 1243, 1098, 779, 692, 613, 456, 390, 340 and 290 $cm^{-1}$. $^1H$ NMR, δ 7.26 (m, 4 H) and 8.26 (m, 4 H).

R = *p*-$ClC_6H_4$. Yield 52% (Found: C, 24.95; H, 1.65. $C_{14}H_8Cl_8Nb_2O_5\cdot 0.125C_6H_{14}$ requires C, 24.05; H, 1.35%). IR: 1516 [$\nu_{asym}(CO_2^-)$], 1493, 1468, 1407 [$\nu_{sym}(CO_2^-)$], 1113, 1092, 1015, 726, 421, 380, 350 and 270 cm$^{-1}$. $^1$H NMR, δ 8.16 (m, 4 H) and 7.51 (m, 4 H), solvent resonances (complex : $C_6H_{14}$ 1 : 0.125) also present.

R = *o*-$ClC_6H_4$. Yield 66% (Found: C, 23.70; H, 1.20; Nb, 26.65. $C_{14}H_8Cl_8Nb_2O_5$ requires C, 23.15; H, 1.10; Nb, 25.60%). IR: 1585, 1567, 1464 [$\nu_{asym}(CO_2^-)$], 1304, 370, 340, 300, 270 and 240 cm$^{-1}$. $^1$H NMR, δ 7.54 (m, 6 H) and 8.22 (m, 2 H).

R = *p*-$MeC_6H_4$. Yield 76% (Found: C, 27.45; H, 2.40. $C_{16}H_8Cl_6Nb_2O_5$ requires C, 28.05; H, 2.05%). IR: 1510, 1473 [$\nu_{asym}(CO_2^-)$], 1411, 1359 [$\nu_{sym}(CO_2^-)$], 754, 467, 410, 380, 320 and 300 cm$^{-1}$. $^1$H NMR, δ 2.47 (m, 6 H), 7.30 (m, 4 H) and 8.12 (m, 4 H).

R = *o*-$BrC_6H_4$. Yield 62% (Found: C, 22.25; H, 1.35. $C_{14}H_8Br_2Cl_6Nb_2O_5{\cdot}0.25C_6H_{14}$ requires C, 22.25; H, 1.40%). IR: 1489 [$\nu_{asym}(CO_2^-)$], 1461, 1397 [$\nu_{sym}(CO_2^-)$], 1294, 1033, 746, 722, 503, 480, 390, 360, 330 and 280 cm$^{-1}$. $^1$H NMR, δ 7.51 (m, 4 H), 7.78 (m, 2 H) and 8.24 (m, 2 H).

R = *o*-$FC_6H_4$. Yield 40% (Found: C, 25.70; H, 1.65. $C_{14}H_8Cl_6F_2Nb_2O_5{\cdot}0.125C_6H_{14}$ requires C, 25.15; H, 1.40%). IR: 1494 [$\nu_{asym}(CO_2^-)$], 1470, 1441, 1403 [$\nu_{sym}(CO_2^-)$], 1233, 759, 430, 390, 345 and 280 cm$^{-1}$. $^1$H NMR, δ 7.22 (m, 4 H), 7.68 (m, 2 H) and 8.16 (m, 2 H), solvent resonances (complex : $C_6H_{14}$ 1 : 0.125) also present.

R = 2,6-$Cl_2C_6H_3$. Yield 26% (Found: C, 21.25; H, 1.00. $C_{14}H_6Cl_{10}Nb_2O_5{\cdot}0.125C_6H_{14}$ requires C, 22.00; H, 0.95%). IR: 1489, 1458 [$\nu_{asym}(CO_2^-)$], 1433, 1396 [$\nu_{sym}(CO_2^-)$], 1243, 1211, 730, 708, 503, 450, 400, 390, 330 and 260 cm$^{-1}$. $^1$H NMR, δ 7.37 (s), solvent resonances (complex : $C_6H_{14}$ 1 : 0.125) also present.

R = *o*-$MeC_6H_4$. Yield 14% (Found: C, 30.05; H, 2.65. $C_{16}H_8Cl_6Nb_2O_5{\cdot}0.25C_6H_{14}$ requires C, 29.75; H, 2.50%). IR: 1498, 1475 [$\nu_{asym}(CO_2^-)$], 1456, 1425 [$\nu_{sym}(CO_2^-)$], 1380, 739, 559, 479, 390 and 320 cm$^{-1}$. $^1$H NMR, δ 8.25 (m), 7.60 (m), 7.34 (m) and 2.79 (s), solvent resonances (complex : $C_6H_{14}$ 1 : 0.25) also present.

*Crystal Data.*—$C_{14}H_{10}Cl_6Nb_2O_5{\cdot}C_nH_{2n+2}$, $M = 656.8 + C_nH_{2n+2}$, monoclinic, space group $P2_1/n$, $a = 9.545(5)$, $b = 17.034(10)$, $c = 16.499(10)$ Å, $\beta = 95.60(4)°$, $U = 2670$ Å$^3$, $Z = 4$, $D_c = 1.63$ g cm$^{-3}$, Mo-Kα radiation, $\lambda = 0.710\,69$ Å, $\mu$(Mo-Kα) = 1.49 mm$^{-1}$, $F(000) = 1472.00$, $T = 290$ K, $R = 0.079$ for 1652 unique observed [$I/\sigma(I) \geqslant 2.0$] reflections. Crystals (yellow plates with poor diffraction at high angle) were obtained from light petroleum (b.p. 60–80 °C)–$CH_2Cl_2$. Data were collected with a Siemens R3m four-circle diffractometer in ω–2θ mode. Maximum 2θ was 45° with scan range ±0.75° (ω) around the $K_{\alpha_1}$–$K_{\alpha_2}$ angles, scan speed 2.5–15° (ω) min$^{-1}$, depending on the intensity of a 2 s pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan time, *hkl* ranges were 0–10, 0–18, −17 to 17. Three standard reflections were monitored every 200 reflections, and showed a slight decrease during data collection (2%). The data were rescaled to correct for this. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 reflections ($18 < 2\theta < 20°$). The reflections collected were processed using a profile analysis to give 1751 unique reflections ($R_{int} = 0.031$), of which 1652 were considered observed [$I/\sigma(I) \geqslant 2.0$]. These were corrected for Lorentz, polarisation and absorption effects (by the Gaussian method); minimum and maximum transmission factors were 0.76 and 0.91. Crystal dimensions were 0.063 × 0.18 × 0.42 mm. Systematic reflection conditions: $h0l$, $h + l = 2n$; $0k0$, $k = 2n$ indicate the space group $P2_1/n$.

The two niobium atoms were located by the Patterson interpretation section of SHELXTL[15] and the light atoms then found by successive Fourier syntheses. The asymmetric unit includes a severely disordered solvent molecule, presumably one of the light petroleum alkanes; it was modelled with difficulty as two 0.5 and eight 0.25 occupancy carbon atoms. Anisotropic thermal parameters were used for all non-H atoms apart from those in the solvent. Hydrogen atoms were given fixed isotropic thermal parameters, $U = 0.08$ Å$^2$. Those in the main molecule were inserted at calculated positions and not refined; those in the solvent were not included. Final refinement was on $F$ by least-squares methods refining 272 parameters. Largest positive and negative peaks on a final Fourier difference synthesis were of height ±1.0 e Å$^{-3}$ in the solvent region. A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ with $g = 0.003$ was used and shown to be satisfactory by a weight analysis. Final $R = 0.079$, $R' = 0.099$, $S = 1.32$, maximum shift/error in final cycle = 0.26. Computing with SHELXTL PLUS[15] on a DEC MicroVax-II. Scattering factors in the analytical form and anomalous dispersion factors are taken from ref. 16. Selected bond lengths and angles are given in Table 1 and final atomic coordinates in Table 2.

Additional data available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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