Electronic Supplementary Material (ESI) for Dalton Transactions


# New Stable Aryl-Substituted Acyclic Imino-*N*-Heterocyclic Carbene: Synthesis, Characterisation and Coordination to Early Transition Metals

*Timothy G. Larocque,*[a] *Anna C. Badaj,*[a] *Sarim Dastgir*[a,b] *and Gino G. Lavoie**[a]

[a] Department of Chemistry, York University, 4700 Keele Street, Toronto, Ontario, M3J 1P3 (Canada).

Fax: +1 416-736-5936; Tel: +1 416-736-2100 Ext. 77728; E-mail: glavoie@yorku.ca

[b] Current address: Department of Chemistry, College of Science, Sultan Qaboos University, P.O. Box 36, Muscat 123, Sultanate of Oman

**Supplementary Material**

**X-ray Data Table of Contents**

Table 1. Crystal data and structure refinement for **2**.

| | | |
|---|---|---|
| Identification code | k09214 | |
| Empirical formula | C25 H31 N3 | |
| Formula weight | 373.53 | |
| Temperature | 150(1) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | P -1 | |
| Unit cell dimensions | a = 8.5723(3) Å | α= 70.656(2)°. |
| | b = 11.8829(7) Å | β= 88.378(3)°. |
| | c = 12.3644(8) Å | γ = 69.372(3)°. |
| Volume | 1106.61(10) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.121 $Mg/m^3$ | |
| Absorption coefficient | 0.066 $mm^{-1}$ | |
| F(000) | 404 | |
| Crystal size | 0.34 x 0.34 x 0.20 $mm^3$ | |
| Theta range for data collection | 2.59 to 27.50°. | |
| Index ranges | -11<=h<=11, -14<=k<=15, -15<=l<=15 | |
| Reflections collected | 10345 | |
| Independent reflections | 4990 [R(int) = 0.0480] | |
| Completeness to theta = 27.50° | 98.1 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.985 and 0.768 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 4990 / 0 / 261 | |
| Goodness-of-fit on $F^2$ | 1.049 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0699, wR2 = 0.1747 | |
| R indices (all data) | R1 = 0.1269, wR2 = 0.2146 | |
| Largest diff. peak and hole | 0.423 and -0.270 $e.Å^{-3}$ | |

Table 2. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for **2**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 7112(2) | 2549(2) | 7943(2) | 36(1) |
| C(2) | 7055(3) | 3033(2) | 5977(2) | 41(1) |
| C(3) | 6784(3) | 4120(2) | 6183(2) | 41(1) |
| C(4) | 7487(2) | 776(2) | 7198(2) | 32(1) |
| C(5) | 8993(2) | -265(2) | 8010(2) | 39(1) |
| C(6) | 5014(2) | 1388(2) | 5985(2) | 33(1) |
| C(7) | 4952(3) | 1623(2) | 4794(2) | 38(1) |
| C(8) | 3450(3) | 2388(2) | 4130(2) | 45(1) |
| C(9) | 2029(3) | 2912(2) | 4618(2) | 49(1) |
| C(10) | 2100(3) | 2662(2) | 5796(2) | 44(1) |
| C(11) | 3591(2) | 1894(2) | 6504(2) | 35(1) |
| C(12) | 6499(3) | 1020(2) | 4265(2) | 48(1) |
| C(13) | 3643(3) | 1581(2) | 7785(2) | 41(1) |
| C(14) | 6493(2) | 4720(2) | 7962(2) | 31(1) |
| C(15) | 4832(2) | 5442(2) | 8040(2) | 35(1) |
| C(16) | 4559(2) | 6313(2) | 8612(2) | 36(1) |
| C(17) | 5862(2) | 6491(2) | 9087(2) | 36(1) |
| C(18) | 7497(2) | 5739(2) | 9003(2) | 34(1) |
| C(19) | 7839(2) | 4853(2) | 8444(2) | 33(1) |
| C(20) | 3381(3) | 5272(2) | 7534(2) | 48(1) |
| C(21) | 5511(3) | 7498(2) | 9640(2) | 48(1) |
| C(22) | 9612(2) | 4078(2) | 8340(2) | 41(1) |
| C(23) | 8561(3) | -484(2) | 9257(2) | 50(1) |
| C(24) | 10518(3) | 143(2) | 7831(3) | 52(1) |
| C(25) | 9374(3) | -1512(2) | 7758(3) | 56(1) |
| N(1) | 7246(2) | 2088(2) | 7042(2) | 33(1) |
| N(2) | 6813(2) | 3805(2) | 7374(2) | 34(1) |
| N(3) | 6513(2) | 482(2) | 6685(2) | 35(1) |

Table 3. Bond lengths [Å] and angles [°] for **2**.

| | |
|---|---|
| C(1)-N(2) | 1.354(3) |
| C(1)-N(1) | 1.380(3) |
| C(2)-C(3) | 1.338(3) |
| C(2)-N(1) | 1.388(3) |
| C(3)-N(2) | 1.393(3) |
| C(4)-N(3) | 1.266(3) |
| C(4)-N(1) | 1.444(3) |
| C(4)-C(5) | 1.526(3) |
| C(5)-C(24) | 1.533(3) |
| C(5)-C(23) | 1.534(3) |
| C(5)-C(25) | 1.535(3) |
| C(6)-C(11) | 1.399(3) |
| C(6)-C(7) | 1.404(3) |
| C(6)-N(3) | 1.425(3) |
| C(7)-C(8) | 1.377(3) |
| C(7)-C(12) | 1.513(3) |
| C(8)-C(9) | 1.382(3) |
| C(9)-C(10) | 1.385(3) |
| C(10)-C(11) | 1.395(3) |
| C(11)-C(13) | 1.500(3) |
| C(14)-C(19) | 1.393(3) |
| C(14)-C(15) | 1.400(3) |
| C(14)-N(2) | 1.445(2) |
| C(15)-C(16) | 1.390(3) |
| C(15)-C(20) | 1.511(3) |
| C(16)-C(17) | 1.387(3) |
| C(17)-C(18) | 1.394(3) |
| C(17)-C(21) | 1.505(3) |
| C(18)-C(19) | 1.388(3) |
| C(19)-C(22) | 1.502(3) |
| | |
| N(2)-C(1)-N(1) | 101.48(19) |
| C(3)-C(2)-N(1) | 106.5(2) |
| C(2)-C(3)-N(2) | 106.1(2) |

| | |
|---|---|
| N(3)-C(4)-N(1) | 122.38(18) |
| N(3)-C(4)-C(5) | 120.47(18) |
| N(1)-C(4)-C(5) | 117.15(17) |
| C(4)-C(5)-C(24) | 109.91(19) |
| C(4)-C(5)-C(23) | 109.01(16) |
| C(24)-C(5)-C(23) | 110.11(19) |
| C(4)-C(5)-C(25) | 108.90(17) |
| C(24)-C(5)-C(25) | 109.93(18) |
| C(23)-C(5)-C(25) | 109.0(2) |
| C(11)-C(6)-C(7) | 121.56(18) |
| C(11)-C(6)-N(3) | 119.69(19) |
| C(7)-C(6)-N(3) | 118.26(17) |
| C(8)-C(7)-C(6) | 118.5(2) |
| C(8)-C(7)-C(12) | 121.3(2) |
| C(6)-C(7)-C(12) | 120.24(19) |
| C(7)-C(8)-C(9) | 121.2(2) |
| C(8)-C(9)-C(10) | 119.9(2) |
| C(9)-C(10)-C(11) | 121.1(2) |
| C(10)-C(11)-C(6) | 117.8(2) |
| C(10)-C(11)-C(13) | 120.84(18) |
| C(6)-C(11)-C(13) | 121.32(18) |
| C(19)-C(14)-C(15) | 121.82(18) |
| C(19)-C(14)-N(2) | 119.37(16) |
| C(15)-C(14)-N(2) | 118.80(17) |
| C(16)-C(15)-C(14) | 117.67(18) |
| C(16)-C(15)-C(20) | 120.91(18) |
| C(14)-C(15)-C(20) | 121.41(19) |
| C(17)-C(16)-C(15) | 122.38(18) |
| C(16)-C(17)-C(18) | 117.98(19) |
| C(16)-C(17)-C(21) | 120.65(18) |
| C(18)-C(17)-C(21) | 121.34(19) |
| C(19)-C(18)-C(17) | 121.95(19) |
| C(18)-C(19)-C(14) | 118.18(17) |
| C(18)-C(19)-C(22) | 120.88(18) |
| C(14)-C(19)-C(22) | 120.93(18) |
| C(1)-N(1)-C(2) | 112.55(18) |

| | |
|---|---|
| C(1)-N(1)-C(4) | 123.25(18) |
| C(2)-N(1)-C(4) | 124.15(17) |
| C(1)-N(2)-C(3) | 113.41(17) |
| C(1)-N(2)-C(14) | 122.37(18) |
| C(3)-N(2)-C(14) | 124.18(18) |
| C(4)-N(3)-C(6) | 123.86(18) |

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **2**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 35(1) | 35(1) | 38(1) | -15(1) | 3(1) | -10(1) |
| C(2) | 56(1) | 40(1) | 32(1) | -13(1) | 5(1) | -22(1) |
| C(3) | 57(1) | 37(1) | 31(1) | -7(1) | 0(1) | -21(1) |
| C(4) | 34(1) | 31(1) | 34(1) | -15(1) | 11(1) | -13(1) |
| C(5) | 34(1) | 31(1) | 47(2) | -12(1) | -2(1) | -8(1) |
| C(6) | 40(1) | 29(1) | 34(1) | -13(1) | 1(1) | -14(1) |
| C(7) | 51(1) | 34(1) | 33(1) | -10(1) | 2(1) | -21(1) |
| C(8) | 59(2) | 42(1) | 36(1) | -8(1) | -3(1) | -26(1) |
| C(9) | 49(1) | 42(2) | 49(2) | -5(1) | -13(1) | -17(1) |
| C(10) | 39(1) | 38(1) | 51(2) | -13(1) | 0(1) | -11(1) |
| C(11) | 35(1) | 33(1) | 39(1) | -14(1) | 3(1) | -13(1) |
| C(12) | 66(2) | 47(2) | 39(2) | -22(1) | 14(1) | -26(1) |
| C(13) | 38(1) | 46(1) | 40(1) | -19(1) | 7(1) | -14(1) |
| C(14) | 35(1) | 25(1) | 30(1) | -8(1) | 3(1) | -9(1) |
| C(15) | 34(1) | 30(1) | 37(1) | -8(1) | 2(1) | -11(1) |
| C(16) | 33(1) | 31(1) | 39(1) | -10(1) | 7(1) | -8(1) |
| C(17) | 45(1) | 32(1) | 31(1) | -11(1) | 8(1) | -14(1) |
| C(18) | 40(1) | 34(1) | 30(1) | -9(1) | 2(1) | -15(1) |
| C(19) | 34(1) | 28(1) | 32(1) | -7(1) | 1(1) | -10(1) |
| C(20) | 35(1) | 44(2) | 66(2) | -18(1) | 0(1) | -13(1) |
| C(21) | 57(1) | 43(1) | 50(2) | -25(1) | 11(1) | -17(1) |
| C(22) | 36(1) | 41(1) | 46(2) | -17(1) | 0(1) | -11(1) |
| C(23) | 59(2) | 40(1) | 43(2) | -3(1) | -11(1) | -18(1) |
| C(24) | 33(1) | 43(2) | 78(2) | -21(1) | -2(1) | -10(1) |
| C(25) | 42(1) | 39(2) | 83(2) | -25(2) | -6(1) | -5(1) |
| N(1) | 35(1) | 32(1) | 35(1) | -14(1) | 3(1) | -13(1) |
| N(2) | 36(1) | 30(1) | 34(1) | -12(1) | 1(1) | -11(1) |
| N(3) | 36(1) | 34(1) | 37(1) | -15(1) | 5(1) | -12(1) |

Table 5. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for **2**.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2) | 7107 | 2929 | 5246 | 50 |
| H(3) | 6608 | 4941 | 5629 | 50 |
| H(8) | 3391 | 2558 | 3323 | 54 |
| H(9) | 1006 | 3443 | 4147 | 59 |
| H(10) | 1116 | 3019 | 6127 | 53 |
| H(12A) | 6185 | 1129 | 3471 | 72 |
| H(12B) | 7009 | 105 | 4715 | 72 |
| H(12C) | 7303 | 1435 | 4268 | 72 |
| H(13A) | 2519 | 1978 | 7990 | 61 |
| H(13B) | 4416 | 1909 | 8035 | 61 |
| H(13C) | 4028 | 650 | 8167 | 61 |
| H(16) | 3439 | 6804 | 8680 | 43 |
| H(18) | 8403 | 5835 | 9340 | 41 |
| H(20A) | 3414 | 5490 | 6699 | 73 |
| H(20B) | 2325 | 5836 | 7696 | 73 |
| H(20C) | 3463 | 4380 | 7880 | 73 |
| H(21A) | 6514 | 7329 | 10120 | 72 |
| H(21B) | 4585 | 7476 | 10120 | 72 |
| H(21C) | 5205 | 8343 | 9040 | 72 |
| H(22A) | 9803 | 3165 | 8691 | 62 |
| H(22B) | 10384 | 4290 | 8737 | 62 |
| H(22C) | 9804 | 4275 | 7525 | 62 |
| H(23A) | 8228 | 325 | 9406 | 75 |
| H(23B) | 9544 | -1116 | 9785 | 75 |
| H(23C) | 7635 | -801 | 9377 | 75 |
| H(24A) | 10697 | 385 | 7012 | 78 |
| H(24B) | 11512 | -572 | 8281 | 78 |
| H(24C) | 10319 | 875 | 8086 | 78 |
| H(25A) | 8386 | -1756 | 7857 | 84 |
| H(25B) | 10318 | -2193 | 8292 | 84 |

| | | | | |
|---|---|---|---|---|
| H(25C) | 9663 | -1382 | 6965 | 84 |

Table 6. Crystal data and structure refinement for **3a**.

| | | |
|---|---|---|
| Identification code | k1010 | |
| Empirical formula | C26 H33 Cl6 N3 Ti | |
| Formula weight | 648.15 | |
| Temperature | 150(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P 21/n | |
| Unit cell dimensions | a = 9.7534(5) Å | α= 90°. |
| | b = 18.8425(11) Å | β= 93.221(3)°. |
| | c = 16.5548(7) Å | γ = 90°. |
| Volume | 3037.6(3) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.417 $Mg/m^3$ | |
| Absorption coefficient | 0.830 $mm^{-1}$ | |
| F(000) | 1336 | |
| Crystal size | 0.15 x 0.06 x 0.04 $mm^3$ | |
| Theta range for data collection | 2.60 to 25.07°. | |
| Index ranges | -11<=h<=11, -20<=k<=22, -19<=l<=19 | |
| Reflections collected | 20804 | |
| Independent reflections | 5388 [R(int) = 0.0855] | |
| Completeness to theta = 25.07° | 99.6 % | |
| Max. and min. transmission | 0.9675 and 0.8856 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 5388 / 18 / 337 | |
| Goodness-of-fit on $F^2$ | 1.020 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0674, wR2 = 0.1630 | |
| R indices (all data) | R1 = 0.1172, wR2 = 0.1886 | |
| Largest diff. peak and hole | 1.290 and -1.080 $e.Å^{-3}$ | |

Table 7. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for **3a**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Ti(1) | 7363(1) | 2869(1) | 2762(1) | 36(1) |
| Cl(3) | 9684(2) | 3011(1) | 2884(1) | 48(1) |
| Cl(2) | 5030(2) | 3034(1) | 2697(1) | 51(1) |
| Cl(4) | 7361(2) | 1968(1) | 1841(1) | 54(1) |
| Cl(1) | 7322(2) | 2316(1) | 3956(1) | 45(1) |
| N(1) | 7457(4) | 4496(2) | 2683(2) | 38(1) |
| N(2) | 7375(4) | 4260(2) | 3951(3) | 39(1) |
| N(3) | 7444(4) | 3675(2) | 1676(2) | 34(1) |
| C(1) | 7395(5) | 3945(3) | 3223(3) | 36(1) |
| C(2) | 7502(6) | 5142(3) | 3092(4) | 48(2) |
| C(3) | 7453(6) | 4987(3) | 3873(4) | 50(2) |
| C(4) | 7493(5) | 4345(3) | 1827(3) | 36(1) |
| C(5) | 7563(6) | 5000(3) | 1280(3) | 41(1) |
| C(24) | 6262(6) | 5461(3) | 1379(4) | 54(2) |
| C(23) | 8918(6) | 5406(3) | 1503(4) | 54(2) |
| C(25) | 7580(7) | 4841(3) | 367(3) | 59(2) |
| C(14) | 7312(6) | 3931(3) | 4742(3) | 39(1) |
| C(19) | 6029(6) | 3838(3) | 5053(3) | 43(1) |
| C(18) | 5997(6) | 3578(3) | 5846(3) | 48(2) |
| C(17) | 7201(7) | 3415(3) | 6306(3) | 50(2) |
| C(16) | 8441(6) | 3509(3) | 5960(3) | 43(1) |
| C(15) | 8537(6) | 3773(3) | 5182(3) | 41(1) |
| C(22) | 4719(6) | 4012(3) | 4573(4) | 56(2) |
| C(21) | 7139(8) | 3159(4) | 7168(3) | 65(2) |
| C(20) | 9916(6) | 3900(3) | 4845(4) | 52(2) |
| C(6) | 7461(6) | 3394(3) | 853(3) | 37(1) |
| C(11) | 6202(6) | 3257(3) | 430(3) | 42(1) |
| C(10) | 6229(7) | 2928(3) | -323(3) | 50(2) |
| C(9) | 7448(7) | 2741(3) | -644(3) | 54(2) |
| C(8) | 8660(7) | 2893(3) | -226(3) | 50(2) |
| C(7) | 8709(6) | 3229(3) | 533(3) | 41(1) |

| | | | | |
|---|---|---|---|---|
| C(13) | 4833(6) | 3474(4) | 733(3) | 53(2) |
| C(12) | 10080(6) | 3409(4) | 928(3) | 52(2) |
| Cl(5) | 1708(3) | 4732(2) | 3309(2) | 134(1) |
| Cl(6) | 2686(2) | 4958(2) | 1730(1) | 114(1) |
| C(1S) | 2491(14) | 4371(6) | 2511(4) | 85(4) |
| C(2S) | 3110(10) | 4816(9) | 2735(3) | 85(4) |

Table 8. Bond lengths [Å] and angles [°] for **3a**.

| | |
|---|---|
| Ti(1)-C(1) | 2.167(5) |
| Ti(1)-Cl(1) | 2.2370(16) |
| Ti(1)-Cl(3) | 2.2775(18) |
| Ti(1)-Cl(4) | 2.2808(16) |
| Ti(1)-Cl(2) | 2.2930(18) |
| Ti(1)-N(3) | 2.358(4) |
| N(1)-C(1) | 1.373(6) |
| N(1)-C(2) | 1.392(7) |
| N(1)-C(4) | 1.448(6) |
| N(2)-C(1) | 1.344(6) |
| N(2)-C(3) | 1.379(7) |
| N(2)-C(14) | 1.453(7) |
| N(3)-C(4) | 1.288(6) |
| N(3)-C(6) | 1.463(6) |
| C(2)-C(3) | 1.329(8) |
| C(4)-C(5) | 1.535(7) |
| C(5)-C(25) | 1.542(8) |
| C(5)-C(23) | 1.552(8) |
| C(5)-C(24) | 1.554(8) |
| C(14)-C(19) | 1.390(8) |
| C(14)-C(15) | 1.396(8) |
| C(19)-C(18) | 1.403(8) |
| C(19)-C(22) | 1.502(8) |
| C(18)-C(17) | 1.397(8) |
| C(17)-C(16) | 1.379(8) |
| C(17)-C(21) | 1.512(8) |
| C(16)-C(15) | 1.388(7) |
| C(15)-C(20) | 1.504(8) |
| C(6)-C(7) | 1.390(8) |
| C(6)-C(11) | 1.403(7) |
| C(11)-C(10) | 1.394(8) |
| C(11)-C(13) | 1.508(8) |
| C(10)-C(9) | 1.375(9) |
| C(9)-C(8) | 1.367(8) |

| | |
|---|---|
| C(8)-C(7) | 1.405(8) |
| C(7)-C(12) | 1.494(8) |
| Cl(5)-C(1S) | 1.704(6) |
| Cl(5)-C(2S) | 1.717(6) |
| Cl(6)-C(2S) | 1.712(6) |
| Cl(6)-C(1S) | 1.721(6) |

| | |
|---|---|
| C(1)-Ti(1)-Cl(1) | 97.19(14) |
| C(1)-Ti(1)-Cl(3) | 82.16(15) |
| Cl(1)-Ti(1)-Cl(3) | 92.49(6) |
| C(1)-Ti(1)-Cl(4) | 158.65(15) |
| Cl(1)-Ti(1)-Cl(4) | 104.16(6) |
| Cl(3)-Ti(1)-Cl(4) | 96.34(7) |
| C(1)-Ti(1)-Cl(2) | 83.34(15) |
| Cl(1)-Ti(1)-Cl(2) | 92.17(6) |
| Cl(3)-Ti(1)-Cl(2) | 165.21(7) |
| Cl(4)-Ti(1)-Cl(2) | 96.11(7) |
| C(1)-Ti(1)-N(3) | 70.42(16) |
| Cl(1)-Ti(1)-N(3) | 167.58(11) |
| Cl(3)-Ti(1)-N(3) | 85.17(11) |
| Cl(4)-Ti(1)-N(3) | 88.23(11) |
| Cl(2)-Ti(1)-N(3) | 87.27(11) |
| C(1)-N(1)-C(2) | 110.2(4) |
| C(1)-N(1)-C(4) | 119.6(4) |
| C(2)-N(1)-C(4) | 130.2(4) |
| C(1)-N(2)-C(3) | 110.5(4) |
| C(1)-N(2)-C(14) | 128.6(4) |
| C(3)-N(2)-C(14) | 120.8(4) |
| C(4)-N(3)-C(6) | 122.3(4) |
| C(4)-N(3)-Ti(1) | 119.1(3) |
| C(6)-N(3)-Ti(1) | 118.6(3) |
| N(2)-C(1)-N(1) | 104.7(4) |
| N(2)-C(1)-Ti(1) | 136.7(4) |
| N(1)-C(1)-Ti(1) | 118.6(3) |
| C(3)-C(2)-N(1) | 106.2(5) |
| C(2)-C(3)-N(2) | 108.3(5) |

| | |
|---|---|
| N(3)-C(4)-N(1) | 112.3(4) |
| N(3)-C(4)-C(5) | 132.6(5) |
| N(1)-C(4)-C(5) | 115.1(4) |
| C(4)-C(5)-C(25) | 115.2(4) |
| C(4)-C(5)-C(23) | 108.7(4) |
| C(25)-C(5)-C(23) | 105.9(5) |
| C(4)-C(5)-C(24) | 108.9(5) |
| C(25)-C(5)-C(24) | 105.4(5) |
| C(23)-C(5)-C(24) | 112.9(5) |
| C(19)-C(14)-C(15) | 122.8(5) |
| C(19)-C(14)-N(2) | 118.1(5) |
| C(15)-C(14)-N(2) | 118.9(5) |
| C(14)-C(19)-C(18) | 117.2(5) |
| C(14)-C(19)-C(22) | 122.2(5) |
| C(18)-C(19)-C(22) | 120.5(5) |
| C(17)-C(18)-C(19) | 121.6(5) |
| C(16)-C(17)-C(18) | 118.4(5) |
| C(16)-C(17)-C(21) | 121.1(6) |
| C(18)-C(17)-C(21) | 120.5(6) |
| C(17)-C(16)-C(15) | 122.5(5) |
| C(16)-C(15)-C(14) | 117.4(5) |
| C(16)-C(15)-C(20) | 120.6(5) |
| C(14)-C(15)-C(20) | 121.9(5) |
| C(7)-C(6)-C(11) | 121.9(5) |
| C(7)-C(6)-N(3) | 119.5(5) |
| C(11)-C(6)-N(3) | 118.4(5) |
| C(10)-C(11)-C(6) | 117.9(5) |
| C(10)-C(11)-C(13) | 118.7(5) |
| C(6)-C(11)-C(13) | 123.4(5) |
| C(9)-C(10)-C(11) | 121.3(6) |
| C(8)-C(9)-C(10) | 119.5(6) |
| C(9)-C(8)-C(7) | 122.1(6) |
| C(6)-C(7)-C(8) | 117.1(5) |
| C(6)-C(7)-C(12) | 124.3(5) |
| C(8)-C(7)-C(12) | 118.6(5) |
| C(1S)-Cl(5)-C(2S) | 37.0(6) |

| | |
|---|---|
| C(2S)-Cl(6)-C(1S) | 36.9(6) |
| Cl(5)-C(1S)-Cl(6) | 113.5(6) |
| Cl(6)-C(2S)-Cl(5) | 113.3(6) |

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Symmetry transformations used to generate equivalent atoms:

Table 9. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **3a**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Ti(1) | 50(1) | 26(1) | 34(1) | 0(1) | 4(1) | 0(1) |
| Cl(3) | 50(1) | 52(1) | 44(1) | 7(1) | 6(1) | 7(1) |
| Cl(2) | 48(1) | 51(1) | 53(1) | 2(1) | 1(1) | -6(1) |
| Cl(4) | 92(1) | 28(1) | 40(1) | -2(1) | 7(1) | 0(1) |
| Cl(1) | 62(1) | 36(1) | 38(1) | 5(1) | 6(1) | 0(1) |
| N(1) | 51(3) | 25(2) | 37(2) | 1(2) | 2(2) | 1(2) |
| N(2) | 45(3) | 34(3) | 38(2) | -5(2) | 6(2) | -1(2) |
| N(3) | 36(2) | 33(2) | 32(2) | 1(2) | 2(2) | 2(2) |
| C(1) | 43(3) | 28(3) | 36(3) | -2(2) | 1(2) | 2(2) |
| C(2) | 71(4) | 24(3) | 50(4) | -8(3) | 5(3) | -4(3) |
| C(3) | 68(4) | 30(3) | 51(4) | -10(3) | 7(3) | -2(3) |
| C(4) | 40(3) | 34(3) | 35(3) | 3(2) | 4(2) | 2(2) |
| C(5) | 51(3) | 30(3) | 44(3) | 9(2) | 5(3) | -1(3) |
| C(24) | 64(4) | 32(3) | 67(4) | 8(3) | 4(3) | 3(3) |
| C(23) | 56(4) | 34(3) | 72(4) | 6(3) | 11(3) | 2(3) |
| C(25) | 85(5) | 42(4) | 49(4) | 18(3) | 6(3) | 0(3) |
| C(14) | 52(4) | 30(3) | 35(3) | -8(2) | 10(3) | 0(3) |
| C(19) | 52(4) | 37(3) | 41(3) | -8(2) | 6(3) | 2(3) |
| C(18) | 50(4) | 46(4) | 50(4) | -5(3) | 16(3) | -6(3) |
| C(17) | 69(4) | 38(3) | 42(3) | -1(3) | 7(3) | -3(3) |
| C(16) | 47(4) | 41(3) | 41(3) | -4(3) | 0(3) | 0(3) |
| C(15) | 45(3) | 36(3) | 42(3) | -9(2) | 7(3) | -3(3) |
| C(22) | 52(4) | 60(4) | 56(4) | -7(3) | 4(3) | 8(3) |
| C(21) | 83(5) | 68(5) | 43(4) | 5(3) | 10(3) | -10(4) |
| C(20) | 53(4) | 52(4) | 51(4) | -4(3) | 5(3) | -6(3) |
| C(6) | 52(4) | 26(3) | 34(3) | 6(2) | 6(3) | 3(2) |
| C(11) | 54(4) | 34(3) | 37(3) | 2(2) | 0(3) | -2(3) |
| C(10) | 65(4) | 50(4) | 34(3) | 2(3) | -5(3) | -3(3) |
| C(9) | 74(5) | 54(4) | 32(3) | 1(3) | 1(3) | 0(3) |
| C(8) | 66(4) | 50(4) | 35(3) | 4(3) | 12(3) | 11(3) |
| C(7) | 53(4) | 37(3) | 33(3) | 6(2) | 5(3) | 5(3) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(13) | 48(4) | 64(4) | 46(3) | 5(3) | -4(3) | 1(3) |
| C(12) | 49(4) | 66(4) | 41(3) | 7(3) | 6(3) | 1(3) |
| Cl(5) | 117(2) | 186(3) | 100(2) | 36(2) | 31(2) | -29(2) |
| Cl(6) | 71(1) | 197(3) | 76(1) | 4(2) | 17(1) | 0(2) |
| C(1S) | 101(8) | 62(7) | 87(7) | -21(6) | -44(6) | 27(6) |
| C(2S) | 101(8) | 62(7) | 87(7) | -21(6) | -44(6) | 27(6) |

Table 10. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for **3a**.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2A) | 7556 | 5601 | 2860 | 58 |
| H(3A) | 7469 | 5320 | 4304 | 59 |
| H(24A) | 5444 | 5193 | 1193 | 81 |
| H(24B) | 6323 | 5895 | 1056 | 81 |
| H(24C) | 6198 | 5587 | 1950 | 81 |
| H(23A) | 9692 | 5147 | 1290 | 80 |
| H(23B) | 9048 | 5443 | 2092 | 80 |
| H(23C) | 8868 | 5882 | 1266 | 80 |
| H(25A) | 8424 | 4585 | 256 | 88 |
| H(25B) | 7543 | 5288 | 63 | 88 |
| H(25C) | 6782 | 4549 | 200 | 88 |
| H(18A) | 5136 | 3510 | 6075 | 58 |
| H(16A) | 9262 | 3389 | 6265 | 52 |
| H(22A) | 4725 | 3786 | 4040 | 84 |
| H(22B) | 4641 | 4527 | 4507 | 84 |
| H(22C) | 3936 | 3835 | 4860 | 84 |
| H(21A) | 7865 | 3389 | 7507 | 97 |
| H(21B) | 7270 | 2643 | 7186 | 97 |
| H(21C) | 6242 | 3278 | 7370 | 97 |
| H(20A) | 10642 | 3746 | 5239 | 78 |
| H(20B) | 10024 | 4407 | 4733 | 78 |
| H(20C) | 9980 | 3630 | 4342 | 78 |
| H(10A) | 5388 | 2832 | -621 | 60 |
| H(9A) | 7446 | 2507 | -1152 | 64 |
| H(8A) | 9498 | 2768 | -456 | 60 |
| H(13A) | 4192 | 3579 | 271 | 80 |
| H(13B) | 4952 | 3898 | 1073 | 80 |
| H(13C) | 4467 | 3086 | 1051 | 80 |
| H(12A) | 9989 | 3822 | 1282 | 77 |
| H(12B) | 10723 | 3521 | 512 | 77 |

| | | | | |
|---|---|---|---|---|
| H(12C) | 10427 | 3004 | 1249 | 77 |
| H(1SA) | 1944 | 3960 | 2304 | 102 |
| H(1SB) | 3407 | 4192 | 2702 | 102 |
| H(2SA) | 3680 | 5217 | 2946 | 102 |
| H(2SB) | 3671 | 4379 | 2791 | 102 |

Table 11. Crystal data and structure refinement for **3b**.

| | | |
|---|---|---|
| Identification code | k10226 | |
| Empirical formula | C29 H39 Cl3 N3 O Ti | |
| Formula weight | 599.88 | |
| Temperature | 150(1) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Tetragonal | |
| Space group | I 41/A | |
| Unit cell dimensions | a = 34.9199(4) Å | α= 90°. |
| | b = 34.9199(4) Å | β= 90°. |
| | c = 11.2791(2) Å | γ = 90°. |
| Volume | 13753.7(3) $Å^3$ | |
| Z | 16 | |
| Density (calculated) | 1.159 $Mg/m^3$ | |
| Absorption coefficient | 0.505 $mm^{-1}$ | |
| F(000) | 5040 | |
| Crystal size | 0.34 x 0.24 x 0.20 mm | |
| Theta range for data collection | 2.61 to 27.50°. | |
| Index ranges | -31<=h<=32, -45<=k<=45, –14<=l<=14 | |
| Reflections collected | 51252 | |
| Independent reflections | 7841 [R(int) = 0.0670] | |
| Completeness to theta = 27.50° | 99.3 % | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 7841 / 0 / 343 | |
| Goodness-of-fit on $F^2$ | 1.115 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0615, wR2 = 0.1605 | |
| R indices (all data) | R1 = 0.0899, wR2 = 0.1788 | |
| Largest diff. peak and hole | 0.475 and -0.425 $e.Å^{-3}$ | |

Table 12. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for **3b**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Ti(1) | 4071(1) | 9100(1) | 1095(1) | 34(1) |
| Cl(2) | 4214(1) | 8603(1) | 2523(1) | 50(1) |
| Cl(1) | 3727(1) | 8708(1) | -170(1) | 53(1) |
| Cl(3) | 3969(1) | 9647(1) | -92(1) | 45(1) |
| N(2) | 4802(1) | 8705(1) | -292(2) | 33(1) |
| N(1) | 4933(1) | 9055(1) | 1221(2) | 31(1) |
| N(3) | 4510(1) | 9445(1) | 2147(2) | 32(1) |
| C(14) | 4614(1) | 8520(1) | -1283(2) | 35(1) |
| O(1) | 3580(1) | 9238(1) | 2146(2) | 48(1) |
| C(6) | 4374(1) | 9787(1) | 2737(3) | 37(1) |
| C(3) | 5187(1) | 8647(1) | -40(3) | 37(1) |
| C(5) | 5202(1) | 9443(1) | 2913(3) | 41(1) |
| C(4) | 4860(1) | 9338(1) | 2110(2) | 32(1) |
| C(11) | 4169(1) | 9760(1) | 3797(3) | 45(1) |
| C(12) | 4678(1) | 10175(1) | 1080(3) | 50(1) |
| C(2) | 5273(1) | 8861(1) | 917(2) | 36(1) |
| C(19) | 4535(1) | 8131(1) | -1188(3) | 40(1) |
| C(24) | 5293(1) | 9076(1) | 3624(3) | 45(1) |
| C(18) | 4376(1) | 7954(1) | -2188(3) | 50(1) |
| C(17) | 4291(1) | 8153(1) | -3211(3) | 52(1) |
| C(15) | 4536(1) | 8733(1) | -2283(3) | 40(1) |
| C(7) | 4432(1) | 10139(1) | 2167(3) | 45(1) |
| C(25) | 5107(1) | 9751(1) | 3838(3) | 51(1) |
| C(8) | 4268(1) | 10465(1) | 2661(4) | 55(1) |
| C(23) | 5551(1) | 9596(1) | 2213(3) | 44(1) |
| C(1) | 4642(1) | 8950(1) | 471(2) | 33(1) |
| C(10) | 4011(1) | 10094(1) | 4257(3) | 61(1) |
| C(13) | 4132(1) | 9387(1) | 4458(3) | 60(1) |
| C(9) | 4057(1) | 10440(1) | 3696(4) | 66(1) |
| C(22) | 4604(1) | 7910(1) | -69(3) | 51(1) |
| C(20) | 4628(1) | 9153(1) | -2377(3) | 53(1) |

| | | | | |
|---|---|---|---|---|
| C(26) | 3327(1) | 8944(1) | 2617(5) | 77(1) |
| C(16) | 4370(1) | 8543(1) | -3246(3) | 47(1) |
| C(29) | 3371(1) | 9597(1) | 2143(3) | 52(1) |
| C(21) | 4118(2) | 7957(1) | -4282(4) | 83(1) |
| C(28) | 3087(1) | 9563(1) | 3136(5) | 90(2) |
| C(27) | 3017(1) | 9143(1) | 3250(5) | 91(2) |

Table 13. Bond lengths [Å] and angles [°] for **3b**.

| | |
|---|---|
| Ti(1)-O(1) | 2.141(2) |
| Ti(1)-C(1) | 2.178(3) |
| Ti(1)-N(3) | 2.282(2) |
| Ti(1)-Cl(1) | 2.3139(9) |
| Ti(1)-Cl(3) | 2.3595(9) |
| Ti(1)-Cl(2) | 2.4202(9) |
| N(2)-C(1) | 1.336(3) |
| N(2)-C(3) | 1.388(4) |
| N(2)-C(14) | 1.448(3) |
| N(1)-C(1) | 1.374(3) |
| N(1)-C(2) | 1.407(3) |
| N(1)-C(4) | 1.431(3) |
| N(3)-C(4) | 1.280(3) |
| N(3)-C(6) | 1.447(3) |
| C(14)-C(15) | 1.379(4) |
| C(14)-C(19) | 1.389(4) |
| O(1)-C(29) | 1.450(4) |
| O(1)-C(26) | 1.455(4) |
| C(6)-C(11) | 1.397(4) |
| C(6)-C(7) | 1.401(5) |
| C(3)-C(2) | 1.347(4) |
| C(5)-C(25) | 1.534(4) |
| C(5)-C(4) | 1.541(4) |
| C(5)-C(24) | 1.544(4) |
| C(5)-C(23) | 1.548(4) |
| C(11)-C(10) | 1.391(5) |
| C(11)-C(13) | 1.505(5) |
| C(12)-C(7) | 1.503(5) |
| C(19)-C(18) | 1.401(4) |
| C(19)-C(22) | 1.499(4) |
| C(18)-C(17) | 1.380(5) |
| C(17)-C(16) | 1.391(5) |
| C(17)-C(21) | 1.515(5) |
| C(15)-C(16) | 1.398(4) |

| | |
|---|---|
| C(15)-C(20) | 1.505(4) |
| C(7)-C(8) | 1.391(4) |
| C(8)-C(9) | 1.383(6) |
| C(10)-C(9) | 1.374(6) |
| C(26)-C(27) | 1.472(6) |
| C(29)-C(28) | 1.501(6) |
| C(28)-C(27) | 1.491(7) |

| | |
|---|---|
| O(1)-Ti(1)-C(1) | 165.15(10) |
| O(1)-Ti(1)-N(3) | 97.52(9) |
| C(1)-Ti(1)-N(3) | 71.37(9) |
| O(1)-Ti(1)-Cl(1) | 93.40(7) |
| C(1)-Ti(1)-Cl(1) | 97.65(8) |
| N(3)-Ti(1)-Cl(1) | 169.00(7) |
| O(1)-Ti(1)-Cl(3) | 90.65(6) |
| C(1)-Ti(1)-Cl(3) | 98.61(8) |
| N(3)-Ti(1)-Cl(3) | 88.21(6) |
| Cl(1)-Ti(1)-Cl(3) | 92.96(3) |
| O(1)-Ti(1)-Cl(2) | 87.58(7) |
| C(1)-Ti(1)-Cl(2) | 81.58(7) |
| N(3)-Ti(1)-Cl(2) | 83.92(6) |
| Cl(1)-Ti(1)-Cl(2) | 95.31(4) |
| Cl(3)-Ti(1)-Cl(2) | 171.63(4) |
| C(1)-N(2)-C(3) | 111.5(2) |
| C(1)-N(2)-C(14) | 126.3(2) |
| C(3)-N(2)-C(14) | 122.1(2) |
| C(1)-N(1)-C(2) | 110.2(2) |
| C(1)-N(1)-C(4) | 118.9(2) |
| C(2)-N(1)-C(4) | 130.8(2) |
| C(4)-N(3)-C(6) | 124.7(2) |
| C(4)-N(3)-Ti(1) | 118.07(18) |
| C(6)-N(3)-Ti(1) | 117.04(17) |
| C(15)-C(14)-C(19) | 123.4(3) |
| C(15)-C(14)-N(2) | 118.8(2) |
| C(19)-C(14)-N(2) | 117.8(3) |
| C(29)-O(1)-C(26) | 107.8(3) |

| | |
|---|---|
| C(29)-O(1)-Ti(1) | 126.60(19) |
| C(26)-O(1)-Ti(1) | 122.0(2) |
| C(11)-C(6)-C(7) | 121.8(3) |
| C(11)-C(6)-N(3) | 120.3(3) |
| C(7)-C(6)-N(3) | 117.7(3) |
| C(2)-C(3)-N(2) | 107.4(2) |
| C(25)-C(5)-C(4) | 113.6(2) |
| C(25)-C(5)-C(24) | 105.8(3) |
| C(4)-C(5)-C(24) | 105.5(2) |
| C(25)-C(5)-C(23) | 106.0(3) |
| C(4)-C(5)-C(23) | 113.0(2) |
| C(24)-C(5)-C(23) | 112.8(3) |
| N(3)-C(4)-N(1) | 113.3(2) |
| N(3)-C(4)-C(5) | 130.6(2) |
| N(1)-C(4)-C(5) | 116.0(2) |
| C(10)-C(11)-C(6) | 117.6(3) |
| C(10)-C(11)-C(13) | 120.5(3) |
| C(6)-C(11)-C(13) | 121.8(3) |
| C(3)-C(2)-N(1) | 106.0(2) |
| C(14)-C(19)-C(18) | 116.6(3) |
| C(14)-C(19)-C(22) | 122.5(3) |
| C(18)-C(19)-C(22) | 120.8(3) |
| C(17)-C(18)-C(19) | 122.4(3) |
| C(18)-C(17)-C(16) | 118.4(3) |
| C(18)-C(17)-C(21) | 121.6(3) |
| C(16)-C(17)-C(21) | 120.0(3) |
| C(14)-C(15)-C(16) | 117.5(3) |
| C(14)-C(15)-C(20) | 122.8(3) |
| C(16)-C(15)-C(20) | 119.7(3) |
| C(8)-C(7)-C(6) | 118.4(3) |
| C(8)-C(7)-C(12) | 119.6(3) |
| C(6)-C(7)-C(12) | 122.0(3) |
| C(9)-C(8)-C(7) | 120.4(4) |
| N(2)-C(1)-N(1) | 104.9(2) |
| N(2)-C(1)-Ti(1) | 138.2(2) |
| N(1)-C(1)-Ti(1) | 114.52(18) |

| | |
|---|---|
| C(9)-C(10)-C(11) | 121.5(4) |
| C(10)-C(9)-C(8) | 120.3(3) |
| O(1)-C(26)-C(27) | 106.8(3) |
| C(17)-C(16)-C(15) | 121.6(3) |
| O(1)-C(29)-C(28) | 105.2(3) |
| C(27)-C(28)-C(29) | 104.6(4) |
| C(26)-C(27)-C(28) | 107.6(3) |

Table 14. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **3b**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Ti(1) | 30(1) | 28(1) | 45(1) | 1(1) | 0(1) | -1(1) |
| Cl(2) | 56(1) | 35(1) | 60(1) | 11(1) | 5(1) | 4(1) |
| Cl(1) | 47(1) | 42(1) | 70(1) | -10(1) | -7(1) | -9(1) |
| Cl(3) | 48(1) | 38(1) | 51(1) | 8(1) | -8(1) | -3(1) |
| N(2) | 35(1) | 33(1) | 31(1) | -7(1) | -2(1) | 5(1) |
| N(1) | 29(1) | 34(1) | 31(1) | -9(1) | -2(1) | 5(1) |
| N(3) | 32(1) | 30(1) | 34(1) | -1(1) | -1(1) | 3(1) |
| C(14) | 37(1) | 31(1) | 36(1) | -10(1) | -4(1) | 2(1) |
| O(1) | 35(1) | 38(1) | 69(2) | 7(1) | 14(1) | 1(1) |
| C(6) | 34(1) | 36(1) | 43(2) | -9(1) | -4(1) | 8(1) |
| C(3) | 37(1) | 37(1) | 36(1) | -6(1) | -2(1) | 5(1) |
| C(5) | 39(2) | 48(2) | 34(1) | -10(1) | -6(1) | 5(1) |
| C(4) | 35(1) | 31(1) | 30(1) | -3(1) | -2(1) | -2(1) |
| C(11) | 42(2) | 55(2) | 39(2) | -12(1) | 0(1) | 11(1) |
| C(12) | 59(2) | 38(2) | 51(2) | 1(1) | -10(2) | -9(1) |
| C(2) | 28(1) | 44(2) | 36(1) | -6(1) | -2(1) | 5(1) |
| C(19) | 40(2) | 37(2) | 42(2) | -11(1) | -2(1) | 6(1) |
| C(24) | 43(2) | 55(2) | 36(2) | -5(1) | -2(1) | 11(1) |
| C(18) | 58(2) | 34(2) | 57(2) | -9(1) | -4(2) | -4(1) |
| C(17) | 60(2) | 54(2) | 41(2) | -13(2) | -10(2) | -5(2) |
| C(15) | 43(2) | 38(2) | 40(2) | -4(1) | -6(1) | -1(1) |
| C(7) | 49(2) | 33(1) | 53(2) | -11(1) | -15(1) | 8(1) |
| C(25) | 44(2) | 64(2) | 46(2) | -28(2) | -14(1) | 12(2) |
| C(8) | 57(2) | 36(2) | 72(2) | -11(2) | -19(2) | 11(1) |
| C(23) | 35(2) | 48(2) | 49(2) | -12(1) | -7(1) | -5(1) |
| C(1) | 34(1) | 33(1) | 32(1) | -1(1) | -2(1) | -1(1) |
| C(10) | 47(2) | 85(3) | 50(2) | -23(2) | -1(2) | 24(2) |
| C(13) | 56(2) | 80(3) | 45(2) | 5(2) | 9(2) | 11(2) |
| C(9) | 57(2) | 60(2) | 82(3) | -32(2) | -17(2) | 27(2) |
| C(22) | 70(2) | 35(2) | 48(2) | 1(1) | -3(2) | 3(2) |
| C(20) | 74(2) | 44(2) | 41(2) | 1(1) | -9(2) | -16(2) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(26) | 63(2) | 52(2) | 115(4) | 15(2) | 45(2) | -11(2) |
| C(16) | 56(2) | 48(2) | 37(2) | -1(1) | -10(1) | 1(1) |
| C(29) | 40(2) | 45(2) | 70(2) | 2(2) | 7(2) | 9(1) |
| C(21) | 107(4) | 76(3) | 65(3) | -22(2) | -30(3) | -16(3) |
| C(28) | 77(3) | 82(3) | 110(4) | 7(3) | 33(3) | 24(3) |
| C(27) | 57(3) | 89(3) | 127(4) | 5(3) | 34(3) | -13(2) |

Table 15. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for **3b**.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2) | 5354 | 8489 | -455 | 44 |
| H(25A) | 4943 | 10169 | 1306 | 74 |
| H(25B) | 4622 | 10412 | 686 | 74 |
| H(25C) | 4626 | 9965 | 553 | 74 |
| H(3) | 5508 | 8877 | 1299 | 43 |
| H(6A) | 5498 | 9127 | 4167 | 67 |
| H(6B) | 5367 | 8876 | 3088 | 67 |
| H(6C) | 5069 | 8998 | 4058 | 67 |
| H(11) | 4326 | 7693 | -2161 | 59 |
| H(8A) | 4905 | 9661 | 4345 | 77 |
| H(8B) | 5026 | 9980 | 3443 | 77 |
| H(8C) | 5330 | 9804 | 4305 | 77 |
| H(22) | 4300 | 10701 | 2292 | 66 |
| H(7A) | 5500 | 9852 | 1948 | 66 |
| H(7B) | 5597 | 9434 | 1540 | 66 |
| H(7C) | 5772 | 9596 | 2717 | 66 |
| H(20) | 3872 | 10083 | 4959 | 73 |
| H(24A) | 4139 | 9436 | 5296 | 91 |
| H(24B) | 4341 | 9221 | 4246 | 91 |
| H(24C) | 3894 | 9267 | 4254 | 91 |
| H(21) | 3946 | 10659 | 4015 | 79 |
| H(15A) | 4491 | 7660 | -141 | 76 |
| H(15B) | 4489 | 8042 | 587 | 76 |
| H(15C) | 4874 | 7885 | 62 | 76 |
| H(17A) | 4462 | 9295 | -1859 | 79 |
| H(17B) | 4590 | 9237 | -3179 | 79 |
| H(17C) | 4889 | 9195 | -2153 | 79 |
| H(26A) | 3466 | 8777 | 3154 | 92 |
| H(26B) | 3223 | 8790 | 1977 | 92 |
| H(13) | 4311 | 8682 | -3927 | 57 |

| | | | | |
|---|---|---|---|---|
| H(29A) | 3241 | 9635 | 1392 | 62 |
| H(29B) | 3543 | 9811 | 2279 | 62 |
| H(16A) | 4045 | 8146 | -4857 | 124 |
| H(16B) | 3896 | 7814 | -4042 | 124 |
| H(16C) | 4303 | 7786 | -4624 | 124 |
| H(28A) | 3190 | 9667 | 3866 | 108 |
| H(28B) | 2851 | 9697 | 2945 | 108 |
| H(27A) | 3015 | 9069 | 4079 | 110 |
| H(27B) | 2771 | 9077 | 2908 | 110 |

Table 16. Crystal data and structure refinement for **4a**.

| | | |
|---|---|---|
| Identification code | k1024a | |
| Empirical formula | C25 H31 Cl4 N3 Zr | |
| Formula weight | 606.55 | |
| Temperature | 150(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhombic | |
| Space group | P n m a | |
| Unit cell dimensions | a = 25.3593(6) Å | α= 90°. |
| | b = 10.6747(9) Å | β= 90°. |
| | c = 16.5496(12) Å | γ = 90°. |
| Volume | 4480.0(5) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 0.899 $Mg/m^3$ | |
| Absorption coefficient | 0.495 $mm^{-1}$ | |
| F(000) | 1240 | |
| Crystal size | 0.20 x 0.18 x 0.09 $mm^3$ | |
| Theta range for data collection | 2.59 to 25.08°. | |
| Index ranges | -30<=h<=30, -12<=k<=12, -19<=l<=19 | |
| Reflections collected | 17689 | |
| Independent reflections | 4139 [R(int) = 0.0898] | |
| Completeness to theta = 25.08° | 98.0 % | |
| Max. and min. transmission | 0.9568 and 0.9074 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 4139 / 0 / 180 | |
| Goodness-of-fit on $F^2$ | 2.491 | |
| Final R indices [I>2sigma(I)] | R1 = 0.2033, wR2 = 0.5724 | |
| R indices (all data) | R1 = 0.2371, wR2 = 0.5922 | |
| Largest diff. peak and hole | 2.713 and -1.076 $e.Å^{-3}$ | |

Table 17. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for **4a**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Zr(1) | 2669(1) | 2500 | 3107(1) | 46(1) |
| Cl(3) | 1954(2) | 2500 | 4058(3) | 83(2) |
| Cl(2) | 2783(2) | 251(4) | 3058(3) | 70(1) |
| Cl(1) | 2256(2) | 2500 | 1813(3) | 72(2) |
| N(2) | 3811(6) | 2500 | 2004(10) | 66(6) |
| N(3) | 3283(6) | 2500 | 4274(8) | 41(4) |
| C(1) | 3540(7) | 2500 | 2727(10) | 35(4) |
| C(3) | 4362(8) | 2500 | 2192(14) | 85(10) |
| C(4) | 3818(7) | 2500 | 4129(11) | 41(4) |
| C(5) | 4261(7) | 2500 | 4708(13) | 45(5) |
| C(6) | 3587(8) | 2500 | 1212(11) | 57(6) |
| C(7) | 3507(5) | 1335(15) | 862(9) | 51(4) |
| C(8) | 3278(6) | 1406(19) | 61(9) | 62(5) |
| C(9) | 3163(8) | 2500 | -279(12) | 47(5) |
| C(10) | 3621(7) | 60(20) | 1216(11) | 88(6) |
| C(11) | 2908(9) | 2500 | -1146(16) | 64(7) |
| C(12) | 3067(7) | 2500 | 5066(12) | 43(5) |
| C(13) | 2942(6) | 1335(16) | 5440(9) | 58(4) |
| C(14) | 2679(6) | 1357(17) | 6143(10) | 58(5) |
| C(15) | 2529(10) | 2500 | 6493(16) | 76(8) |
| C(16) | 3112(7) | 141(15) | 5081(9) | 62(4) |
| C(17) | 4086(8) | 2500 | 5647(11) | 48(5) |
| C(18) | 4608(7) | 1263(17) | 4666(12) | 74(5) |
| N(1) | 3936(5) | 2500 | 3332(9) | 41(4) |
| C(2) | 4417(9) | 2500 | 2907(14) | 95(11) |

Table 18. Bond lengths [Å] and angles [°] for **4a**.

| | |
|---|---|
| Zr(1)-C(1) | 2.297(17) |
| Zr(1)-Cl(1) | 2.385(5) |
| Zr(1)-Cl(3) | 2.401(5) |
| Zr(1)-Cl(2) | 2.419(5) |
| Zr(1)-Cl(2)#1 | 2.419(5) |
| Zr(1)-N(3) | 2.479(14) |
| N(2)-C(1) | 1.38(2) |
| N(2)-C(3) | 1.43(3) |
| N(2)-C(6) | 1.43(2) |
| N(3)-C(4) | 1.38(2) |
| N(3)-C(12) | 1.42(3) |
| C(1)-N(1) | 1.42(2) |
| C(3)-C(2) | 1.19(3) |
| C(4)-N(1) | 1.35(2) |
| C(4)-C(5) | 1.48(3) |
| C(5)-C(18) | 1.589(19) |
| C(5)-C(18)#1 | 1.589(19) |
| C(5)-C(17) | 1.62(3) |
| C(6)-C(7) | 1.386(18) |
| C(6)-C(7)#1 | 1.386(18) |
| C(7)-C(8) | 1.45(2) |
| C(7)-C(10) | 1.51(2) |
| C(8)-C(9) | 1.33(2) |
| C(9)-C(8)#1 | 1.33(2) |
| C(9)-C(11) | 1.57(3) |
| C(12)-C(13) | 1.425(18) |
| C(12)-C(13)#1 | 1.425(18) |
| C(13)-C(14) | 1.34(2) |
| C(13)-C(16) | 1.47(2) |
| C(14)-C(15) | 1.40(2) |
| C(15)-C(14)#1 | 1.40(2) |
| N(1)-C(2) | 1.41(3) |

| | |
|---|---|
| C(1)-Zr(1)-Cl(1) | 100.1(4) |
| C(1)-Zr(1)-Cl(3) | 155.0(4) |
| Cl(1)-Zr(1)-Cl(3) | 104.9(2) |
| C(1)-Zr(1)-Cl(2) | 82.85(13) |
| Cl(1)-Zr(1)-Cl(2) | 91.25(11) |
| Cl(3)-Zr(1)-Cl(2) | 96.48(12) |
| C(1)-Zr(1)-Cl(2)#1 | 82.85(13) |
| Cl(1)-Zr(1)-Cl(2)#1 | 91.25(11) |
| Cl(3)-Zr(1)-Cl(2)#1 | 96.48(12) |
| Cl(2)-Zr(1)-Cl(2)#1 | 165.7(3) |
| C(1)-Zr(1)-N(3) | 67.0(5) |
| Cl(1)-Zr(1)-N(3) | 167.2(4) |
| Cl(3)-Zr(1)-N(3) | 87.9(4) |
| Cl(2)-Zr(1)-N(3) | 87.22(11) |
| Cl(2)#1-Zr(1)-N(3) | 87.22(11) |
| C(1)-N(2)-C(3) | 107.3(16) |
| C(1)-N(2)-C(6) | 126.8(16) |
| C(3)-N(2)-C(6) | 126.0(18) |
| C(4)-N(3)-C(12) | 122.6(14) |
| C(4)-N(3)-Zr(1) | 118.8(11) |
| C(12)-N(3)-Zr(1) | 118.5(10) |
| N(2)-C(1)-N(1) | 105.1(14) |
| N(2)-C(1)-Zr(1) | 135.7(12) |
| N(1)-C(1)-Zr(1) | 119.2(11) |
| C(2)-C(3)-N(2) | 109.3(19) |
| N(1)-C(4)-N(3) | 112.8(15) |
| N(1)-C(4)-C(5) | 117.7(16) |
| N(3)-C(4)-C(5) | 129.5(16) |
| C(4)-C(5)-C(18) | 113.1(11) |
| C(4)-C(5)-C(18)#1 | 113.1(11) |
| C(18)-C(5)-C(18)#1 | 112.5(18) |
| C(4)-C(5)-C(17) | 114.6(15) |
| C(18)-C(5)-C(17) | 101.2(12) |
| C(18)#1-C(5)-C(17) | 101.2(12) |
| C(7)-C(6)-C(7)#1 | 127.6(17) |

| | |
|---|---|
| C(7)-C(6)-N(2) | 116.1(9) |
| C(7)#1-C(6)-N(2) | 116.1(9) |
| C(6)-C(7)-C(8) | 113.1(14) |
| C(6)-C(7)-C(10) | 128.2(14) |
| C(8)-C(7)-C(10) | 118.7(16) |
| C(9)-C(8)-C(7) | 121.5(17) |
| C(8)-C(9)-C(8)#1 | 123(2) |
| C(8)-C(9)-C(11) | 118.5(11) |
| C(8)#1-C(9)-C(11) | 118.5(11) |
| C(13)-C(12)-C(13)#1 | 122(2) |
| C(13)-C(12)-N(3) | 119.1(10) |
| C(13)#1-C(12)-N(3) | 119.1(10) |
| C(14)-C(13)-C(12) | 118.2(16) |
| C(14)-C(13)-C(16) | 120.8(15) |
| C(12)-C(13)-C(16) | 121.0(14) |
| C(13)-C(14)-C(15) | 120.5(17) |
| C(14)-C(15)-C(14)#1 | 121(2) |
| C(4)-N(1)-C(2) | 132.7(17) |
| C(4)-N(1)-C(1) | 122.1(14) |
| C(2)-N(1)-C(1) | 105.1(16) |
| C(3)-C(2)-N(1) | 113(2) |

---

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+1/2,z

Table 19. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **4a**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Zr(1) | 31(1) | 72(2) | 36(1) | 0 | -1(1) | 0 |
| Cl(3) | 36(3) | 171(7) | 43(3) | 0 | 4(2) | 0 |
| Cl(2) | 92(3) | 65(3) | 52(2) | -1(2) | -7(2) | -15(2) |
| Cl(1) | 50(3) | 130(6) | 38(3) | 0 | -11(2) | 0 |
| N(2) | 27(9) | 127(18) | 42(10) | 0 | -13(7) | 0 |
| N(3) | 38(8) | 58(10) | 26(8) | 0 | -2(6) | 0 |
| C(1) | 40(10) | 40(11) | 26(9) | 0 | -2(7) | 0 |
| C(3) | 28(11) | 190(30) | 39(13) | 0 | 14(9) | 0 |
| C(4) | 40(10) | 43(11) | 40(10) | 0 | -6(8) | 0 |
| C(5) | 44(10) | 40(11) | 52(12) | 0 | 5(9) | 0 |
| C(6) | 57(13) | 100(20) | 15(9) | 0 | -11(8) | 0 |
| C(7) | 30(7) | 80(12) | 42(8) | 12(8) | 3(6) | -4(6) |
| C(8) | 45(8) | 104(14) | 38(8) | 2(9) | -1(6) | -12(8) |
| C(9) | 46(11) | 58(14) | 37(10) | 0 | -1(8) | 0 |
| C(10) | 78(12) | 135(18) | 51(9) | 20(12) | -1(9) | 43(12) |
| C(11) | 47(12) | 59(14) | 86(17) | 0 | -41(12) | 0 |
| C(12) | 26(8) | 57(12) | 46(11) | 0 | -13(8) | 0 |
| C(13) | 44(8) | 81(12) | 48(9) | 21(8) | -4(7) | -12(7) |
| C(14) | 56(9) | 78(13) | 41(9) | 9(8) | -13(7) | -18(8) |
| C(15) | 55(13) | 130(30) | 48(14) | 0 | 13(12) | 0 |
| C(16) | 84(12) | 64(11) | 39(8) | -1(8) | -11(8) | -2(9) |
| C(17) | 46(11) | 66(14) | 32(10) | 0 | -7(8) | 0 |
| C(18) | 62(10) | 76(13) | 83(13) | -16(10) | -4(9) | 10(8) |
| N(1) | 23(7) | 64(11) | 36(8) | 0 | 1(6) | 0 |
| C(2) | 30(11) | 220(40) | 38(14) | 0 | 17(9) | 0 |

Table 20. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for **4a**.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(3) | 4640 | 2500 | 1808 | 102 |
| H(8) | 3208 | 655 | -226 | 75 |
| H(10A) | 3886 | 142 | 1643 | 132 |
| H(10B) | 3754 | -494 | 792 | 132 |
| H(10C) | 3296 | -288 | 1444 | 132 |
| H(11A) | 3174 | 2741 | -1547 | 96 |
| H(11B) | 2615 | 3099 | -1161 | 96 |
| H(11C) | 2775 | 1660 | -1271 | 96 |
| H(14) | 2594 | 592 | 6406 | 70 |
| H(15) | 2323 | 2500 | 6973 | 91 |
| H(16A) | 3146 | -493 | 5506 | 94 |
| H(16B) | 3454 | 256 | 4813 | 94 |
| H(16C) | 2851 | -137 | 4683 | 94 |
| H(17A) | 4368 | 2130 | 5975 | 73 |
| H(17B) | 3763 | 2007 | 5711 | 73 |
| H(17C) | 4022 | 3363 | 5824 | 73 |
| H(18A) | 4920 | 1360 | 5010 | 111 |
| H(18B) | 4719 | 1115 | 4107 | 111 |
| H(18C) | 4399 | 548 | 4856 | 111 |
| H(2) | 4751 | 2500 | 3165 | 114 |

Table 21. Crystal data and structure refinement for **6b**.

| | | |
|---|---|---|
| Identification code | edwin_0m | |
| Empirical formula | C30 H41 Cl5 Cr N3 O | |
| Formula weight | 688.91 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Tetragonal | |
| Space group | I4(1)/a | |
| Unit cell dimensions | a = 34.553(6) Å | α= 90°. |
| | b = 34.553 Å | β= 90°. |
| | c = 11.316(2) Å | γ = 90°. |
| Volume | 13510(3) $Å^3$ | |
| Z | 16 | |
| Density (calculated) | 1.355 $Mg/m^3$ | |
| Absorption coefficient | 0.762 $mm^{-1}$ | |
| F(000) | 5744 | |
| Crystal size | 0.349 x 0.101 x 0.083 $mm^3$ | |
| Theta range for data collection | 1.89 to 24.99°. | |
| Index ranges | -31<=h<=41, -41<=k<=33, -13<=l<=13 | |
| Reflections collected | 62831 | |
| Independent reflections | 5953 [R(int) = 0.1289] | |
| Completeness to theta = 24.99° | 100.0 % | |
| Absorption correction | Numerical | |
| Max. and min. transmission | 0.9759 and 0.8123 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 5953 / 12 / 396 | |
| Goodness-of-fit on $F^2$ | 1.372 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0595, wR2 = 0.1178 | |
| R indices (all data) | R1 = 0.0942, wR2 = 0.1291 | |
| Largest diff. peak and hole | 0.583 and -0.619 $e.Å^{-3}$ | |

Table 22. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for **6b**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Cr(1) | 891(1) | 899(1) | 1174(1) | 19(1) |
| Cl(2) | 758(1) | 1404(1) | 2518(1) | 29(1) |
| Cl(1) | 1263(1) | 1295(1) | 5(1) | 29(1) |
| Cl(3) | 979(1) | 387(1) | -91(1) | 25(1) |
| O(1) | 1378(1) | 747(1) | 2184(3) | 30(1) |
| N(1) | 58(1) | 942(1) | 1212(3) | 17(1) |
| N(2) | 212(1) | 1304(1) | -275(3) | 17(1) |
| N(3) | 482(1) | 555(1) | 2156(3) | 20(1) |
| C(1) | 364(1) | 1052(1) | 503(4) | 16(1) |
| C(2) | -280(1) | 1140(1) | 868(4) | 20(1) |
| C(3) | -182(1) | 1360(1) | -60(4) | 19(1) |
| C(4) | 124(1) | 658(1) | 2100(4) | 17(1) |
| C(5) | -219(1) | 548(1) | 2888(4) | 23(1) |
| C(24) | -314(1) | 921(1) | 3602(4) | 26(1) |
| C(23) | -571(1) | 395(1) | 2181(4) | 27(1) |
| C(25) | -124(1) | 238(1) | 3817(4) | 33(1) |
| C(14) | 408(1) | 1491(1) | -1258(4) | 18(1) |
| C(19) | 488(1) | 1887(1) | -1162(4) | 21(1) |
| C(18) | 646(1) | 2068(1) | -2147(4) | 28(1) |
| C(17) | 730(1) | 1865(1) | -3184(4) | 27(1) |
| C(16) | 649(1) | 1472(1) | -3227(4) | 28(1) |
| C(15) | 483(1) | 1278(1) | -2265(4) | 22(1) |
| C(22) | 412(1) | 2106(1) | -29(4) | 27(1) |
| C(21) | 900(2) | 2069(2) | -4242(5) | 44(1) |
| C(20) | 381(1) | 856(1) | -2372(4) | 30(1) |
| C(6) | 624(1) | 209(1) | 2744(4) | 24(1) |
| C(11) | 834(1) | 238(1) | 3793(4) | 30(1) |
| C(10) | 999(1) | -100(2) | 4251(5) | 42(1) |
| C(9) | 955(1) | -451(2) | 3683(5) | 46(2) |
| C(8) | 741(1) | -474(1) | 2659(5) | 38(1) |
| C(7) | 567(1) | -147(1) | 2164(4) | 28(1) |

| | | | | |
|---|---|---|---|---|
| C(13) | 862(2) | 610(2) | 4474(5) | 43(1) |
| C(12) | 315(1) | -186(1) | 1094(4) | 31(1) |
| C(26) | 1606(1) | 397(1) | 2009(5) | 35(1) |
| C(27) | 1901(2) | 406(2) | 3003(6) | 58(2) |
| C(28) | 1981(2) | 837(2) | 3124(7) | 68(2) |
| C(29) | 1636(2) | 1042(1) | 2688(6) | 59(2) |
| C(30) | 1995(3) | 9208(3) | 5520(11) | 77(3) |
| Cl(4) | 1915(1) | 9233(1) | 3991(3) | 87(1) |
| Cl(5) | 2013(1) | 9670(1) | 6083(3) | 109(1) |
| C(30A) | 1819(10) | 9270(11) | 5710(30) | 77(3) |
| Cl(4A) | 1900(3) | 9017(3) | 4385(9) | 87(1) |
| Cl(5A) | 2274(4) | 9570(3) | 6126(10) | 109(1) |

Table 23. Bond lengths [Å] and angles [°] for **6b**.

| | |
|---|---|
| Cr(1)-C(1) | 2.041(4) |
| Cr(1)-O(1) | 2.100(3) |
| Cr(1)-N(3) | 2.156(3) |
| Cr(1)-Cl(1) | 2.2954(13) |
| Cr(1)-Cl(3) | 2.2985(12) |
| Cr(1)-Cl(2) | 2.3596(12) |
| O(1)-C(26) | 1.458(5) |
| O(1)-C(29) | 1.469(5) |
| N(1)-C(1) | 1.380(5) |
| N(1)-C(2) | 1.408(5) |
| N(1)-C(4) | 1.424(5) |
| N(2)-C(1) | 1.345(5) |
| N(2)-C(3) | 1.396(5) |
| N(2)-C(14) | 1.453(5) |
| N(3)-C(4) | 1.287(5) |
| N(3)-C(6) | 1.454(5) |
| C(2)-C(3) | 1.340(6) |
| C(2)-H(2) | 0.9500 |
| C(3)-H(3) | 0.9500 |
| C(4)-C(5) | 1.533(6) |
| C(5)-C(25) | 1.537(6) |
| C(5)-C(23) | 1.546(6) |
| C(5)-C(24) | 1.555(6) |
| C(24)-H(6A) | 0.9800 |
| C(24)-H(6B) | 0.9800 |
| C(24)-H(6C) | 0.9800 |
| C(23)-H(7A) | 0.9800 |
| C(23)-H(7B) | 0.9800 |
| C(23)-H(7C) | 0.9800 |
| C(25)-H(8A) | 0.9800 |
| C(25)-H(8B) | 0.9800 |
| C(25)-H(8C) | 0.9800 |
| C(14)-C(15) | 1.381(6) |
| C(14)-C(19) | 1.401(5) |

| | |
|---|---|
| C(19)-C(18) | 1.388(6) |
| C(19)-C(22) | 1.512(6) |
| C(18)-C(17) | 1.396(6) |
| C(18)-H(11) | 0.9500 |
| C(17)-C(16) | 1.387(6) |
| C(17)-C(21) | 1.508(6) |
| C(16)-C(15) | 1.401(6) |
| C(16)-H(13) | 0.9500 |
| C(15)-C(20) | 1.506(5) |
| C(22)-H(15A) | 0.9800 |
| C(22)-H(15B) | 0.9800 |
| C(22)-H(15C) | 0.9800 |
| C(21)-H(16A) | 0.9800 |
| C(21)-H(16B) | 0.9800 |
| C(21)-H(16C) | 0.9800 |
| C(20)-H(17A) | 0.9800 |
| C(20)-H(17B) | 0.9800 |
| C(20)-H(17C) | 0.9800 |
| C(6)-C(11) | 1.394(6) |
| C(6)-C(7) | 1.410(6) |
| C(11)-C(10) | 1.397(6) |
| C(11)-C(13) | 1.501(7) |
| C(10)-C(9) | 1.382(8) |
| C(10)-H(20) | 0.9500 |
| C(9)-C(8) | 1.375(8) |
| C(9)-H(21) | 0.9500 |
| C(8)-C(7) | 1.397(6) |
| C(8)-H(22) | 0.9500 |
| C(7)-C(12) | 1.497(7) |
| C(13)-H(24A) | 0.9800 |
| C(13)-H(24B) | 0.9800 |
| C(13)-H(24C) | 0.9800 |
| C(12)-H(25A) | 0.9800 |
| C(12)-H(25B) | 0.9800 |
| C(12)-H(25C) | 0.9800 |
| C(26)-C(27) | 1.520(7) |

| | |
|---|---|
| C(26)-H(26A) | 0.9900 |
| C(26)-H(26B) | 0.9900 |
| C(27)-C(28) | 1.523(8) |
| C(27)-H(27A) | 0.9900 |
| C(27)-H(27B) | 0.9900 |
| C(28)-C(29) | 1.471(7) |
| C(28)-H(28A) | 0.9900 |
| C(28)-H(28B) | 0.9900 |
| C(29)-H(29A) | 0.9900 |
| C(29)-H(29B) | 0.9900 |
| C(30)-Cl(5) | 1.718(13) |
| C(30)-Cl(4) | 1.754(13) |
| C(30)-H(30A) | 0.9900 |
| C(30)-H(30B) | 0.9900 |
| C(30A)-Cl(4A) | 1.75(4) |
| C(30A)-Cl(5A) | 1.94(4) |
| C(30A)-H(30C) | 0.9900 |
| C(30A)-H(30D) | 0.9900 |

| | |
|---|---|
| C(1)-Cr(1)-O(1) | 168.84(15) |
| C(1)-Cr(1)-N(3) | 75.50(14) |
| O(1)-Cr(1)-N(3) | 96.10(13) |
| C(1)-Cr(1)-Cl(1) | 97.53(11) |
| O(1)-Cr(1)-Cl(1) | 90.83(9) |
| N(3)-Cr(1)-Cl(1) | 173.03(10) |
| C(1)-Cr(1)-Cl(3) | 94.86(11) |
| O(1)-Cr(1)-Cl(3) | 92.28(9) |
| N(3)-Cr(1)-Cl(3) | 89.00(9) |
| Cl(1)-Cr(1)-Cl(3) | 91.48(5) |
| C(1)-Cr(1)-Cl(2) | 82.82(11) |
| O(1)-Cr(1)-Cl(2) | 89.50(9) |
| N(3)-Cr(1)-Cl(2) | 86.99(9) |
| Cl(1)-Cr(1)-Cl(2) | 92.33(5) |
| Cl(3)-Cr(1)-Cl(2) | 175.77(5) |
| C(26)-O(1)-C(29) | 107.4(3) |
| C(26)-O(1)-Cr(1) | 124.6(3) |

| | |
|---|---|
| C(29)-O(1)-Cr(1) | 121.6(3) |
| C(1)-N(1)-C(2) | 110.0(3) |
| C(1)-N(1)-C(4) | 118.5(3) |
| C(2)-N(1)-C(4) | 131.5(3) |
| C(1)-N(2)-C(3) | 110.9(3) |
| C(1)-N(2)-C(14) | 127.4(3) |
| C(3)-N(2)-C(14) | 121.6(3) |
| C(4)-N(3)-C(6) | 125.1(3) |
| C(4)-N(3)-Cr(1) | 116.9(3) |
| C(6)-N(3)-Cr(1) | 117.8(2) |
| N(2)-C(1)-N(1) | 105.0(3) |
| N(2)-C(1)-Cr(1) | 139.3(3) |
| N(1)-C(1)-Cr(1) | 113.3(3) |
| C(3)-C(2)-N(1) | 106.3(3) |
| C(3)-C(2)-H(2) | 126.8 |
| N(1)-C(2)-H(2) | 126.8 |
| C(2)-C(3)-N(2) | 107.8(3) |
| C(2)-C(3)-H(3) | 126.1 |
| N(2)-C(3)-H(3) | 126.1 |
| N(3)-C(4)-N(1) | 112.3(3) |
| N(3)-C(4)-C(5) | 130.3(4) |
| N(1)-C(4)-C(5) | 117.3(3) |
| C(4)-C(5)-C(25) | 113.9(3) |
| C(4)-C(5)-C(23) | 113.1(3) |
| C(25)-C(5)-C(23) | 106.5(4) |
| C(4)-C(5)-C(24) | 105.0(3) |
| C(25)-C(5)-C(24) | 105.5(3) |
| C(23)-C(5)-C(24) | 112.8(3) |
| C(5)-C(24)-H(6A) | 109.5 |
| C(5)-C(24)-H(6B) | 109.5 |
| H(6A)-C(24)-H(6B) | 109.5 |
| C(5)-C(24)-H(6C) | 109.5 |
| H(6A)-C(24)-H(6C) | 109.5 |
| H(6B)-C(24)-H(6C) | 109.5 |
| C(5)-C(23)-H(7A) | 109.5 |
| C(5)-C(23)-H(7B) | 109.5 |

| | |
|---|---|
| H(7A)-C(23)-H(7B) | 109.5 |
| C(5)-C(23)-H(7C) | 109.5 |
| H(7A)-C(23)-H(7C) | 109.5 |
| H(7B)-C(23)-H(7C) | 109.5 |
| C(5)-C(25)-H(8A) | 109.5 |
| C(5)-C(25)-H(8B) | 109.5 |
| H(8A)-C(25)-H(8B) | 109.5 |
| C(5)-C(25)-H(8C) | 109.5 |
| H(8A)-C(25)-H(8C) | 109.5 |
| H(8B)-C(25)-H(8C) | 109.5 |
| C(15)-C(14)-C(19) | 123.2(4) |
| C(15)-C(14)-N(2) | 118.8(3) |
| C(19)-C(14)-N(2) | 117.9(4) |
| C(18)-C(19)-C(14) | 117.0(4) |
| C(18)-C(19)-C(22) | 121.6(4) |
| C(14)-C(19)-C(22) | 121.3(4) |
| C(19)-C(18)-C(17) | 122.1(4) |
| C(19)-C(18)-H(11) | 118.9 |
| C(17)-C(18)-H(11) | 118.9 |
| C(16)-C(17)-C(18) | 118.5(4) |
| C(16)-C(17)-C(21) | 120.5(4) |
| C(18)-C(17)-C(21) | 121.0(4) |
| C(17)-C(16)-C(15) | 121.6(4) |
| C(17)-C(16)-H(13) | 119.2 |
| C(15)-C(16)-H(13) | 119.2 |
| C(14)-C(15)-C(16) | 117.6(4) |
| C(14)-C(15)-C(20) | 122.6(4) |
| C(16)-C(15)-C(20) | 119.8(4) |
| C(19)-C(22)-H(15A) | 109.5 |
| C(19)-C(22)-H(15B) | 109.5 |
| H(15A)-C(22)-H(15B) | 109.5 |
| C(19)-C(22)-H(15C) | 109.5 |
| H(15A)-C(22)-H(15C) | 109.5 |
| H(15B)-C(22)-H(15C) | 109.5 |
| C(17)-C(21)-H(16A) | 109.5 |
| C(17)-C(21)-H(16B) | 109.5 |

| | |
|---|---|
| H(16A)-C(21)-H(16B) | 109.5 |
| C(17)-C(21)-H(16C) | 109.5 |
| H(16A)-C(21)-H(16C) | 109.5 |
| H(16B)-C(21)-H(16C) | 109.5 |
| C(15)-C(20)-H(17A) | 109.5 |
| C(15)-C(20)-H(17B) | 109.5 |
| H(17A)-C(20)-H(17B) | 109.5 |
| C(15)-C(20)-H(17C) | 109.5 |
| H(17A)-C(20)-H(17C) | 109.5 |
| H(17B)-C(20)-H(17C) | 109.5 |
| C(11)-C(6)-C(7) | 122.1(4) |
| C(11)-C(6)-N(3) | 120.5(4) |
| C(7)-C(6)-N(3) | 117.3(4) |
| C(6)-C(11)-C(10) | 118.0(5) |
| C(6)-C(11)-C(13) | 122.1(4) |
| C(10)-C(11)-C(13) | 119.8(5) |
| C(9)-C(10)-C(11) | 121.0(5) |
| C(9)-C(10)-H(20) | 119.5 |
| C(11)-C(10)-H(20) | 119.5 |
| C(8)-C(9)-C(10) | 120.2(5) |
| C(8)-C(9)-H(21) | 119.9 |
| C(10)-C(9)-H(21) | 119.9 |
| C(9)-C(8)-C(7) | 121.5(5) |
| C(9)-C(8)-H(22) | 119.3 |
| C(7)-C(8)-H(22) | 119.3 |
| C(8)-C(7)-C(6) | 117.3(5) |
| C(8)-C(7)-C(12) | 120.3(4) |
| C(6)-C(7)-C(12) | 122.4(4) |
| C(11)-C(13)-H(24A) | 109.5 |
| C(11)-C(13)-H(24B) | 109.5 |
| H(24A)-C(13)-H(24B) | 109.5 |
| C(11)-C(13)-H(24C) | 109.5 |
| H(24A)-C(13)-H(24C) | 109.5 |
| H(24B)-C(13)-H(24C) | 109.5 |
| C(7)-C(12)-H(25A) | 109.5 |
| C(7)-C(12)-H(25B) | 109.5 |

| | |
|---|---|
| H(25A)-C(12)-H(25B) | 109.5 |
| C(7)-C(12)-H(25C) | 109.5 |
| H(25A)-C(12)-H(25C) | 109.5 |
| H(25B)-C(12)-H(25C) | 109.5 |
| O(1)-C(26)-C(27) | 104.3(4) |
| O(1)-C(26)-H(26A) | 110.9 |
| C(27)-C(26)-H(26A) | 110.9 |
| O(1)-C(26)-H(26B) | 110.9 |
| C(27)-C(26)-H(26B) | 110.9 |
| H(26A)-C(26)-H(26B) | 108.9 |
| C(28)-C(27)-C(26) | 102.0(4) |
| C(28)-C(27)-H(27A) | 111.4 |
| C(26)-C(27)-H(27A) | 111.4 |
| C(28)-C(27)-H(27B) | 111.4 |
| C(26)-C(27)-H(27B) | 111.4 |
| H(27A)-C(27)-H(27B) | 109.2 |
| C(29)-C(28)-C(27) | 107.0(4) |
| C(29)-C(28)-H(28A) | 110.3 |
| C(27)-C(28)-H(28A) | 110.3 |
| C(29)-C(28)-H(28B) | 110.3 |
| C(27)-C(28)-H(28B) | 110.3 |
| H(28A)-C(28)-H(28B) | 108.6 |
| O(1)-C(29)-C(28) | 106.9(4) |
| O(1)-C(29)-H(29A) | 110.3 |
| C(28)-C(29)-H(29A) | 110.3 |
| O(1)-C(29)-H(29B) | 110.3 |
| C(28)-C(29)-H(29B) | 110.3 |
| H(29A)-C(29)-H(29B) | 108.6 |
| Cl(5)-C(30)-Cl(4) | 109.0(7) |
| Cl(5)-C(30)-H(30A) | 109.9 |
| Cl(4)-C(30)-H(30A) | 109.9 |
| Cl(5)-C(30)-H(30B) | 109.9 |
| Cl(4)-C(30)-H(30B) | 109.9 |
| H(30A)-C(30)-H(30B) | 108.3 |
| Cl(4A)-C(30A)-Cl(5A) | 110.3(18) |
| Cl(4A)-C(30A)-H(30C) | 109.6 |

| | |
|---|---|
| Cl(5A)-C(30A)-H(30C) | 109.6 |
| Cl(4A)-C(30A)-H(30D) | 109.6 |
| Cl(5A)-C(30A)-H(30D) | 109.6 |
| H(30C)-C(30A)-H(30D) | 108.1 |

Table 24. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **6b**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Cr(1) | 19(1) | 15(1) | 24(1) | -2(1) | -3(1) | 1(1) |
| Cl(2) | 36(1) | 19(1) | 31(1) | -7(1) | -5(1) | 4(1) |
| Cl(1) | 24(1) | 21(1) | 41(1) | 0(1) | 4(1) | -5(1) |
| Cl(3) | 25(1) | 21(1) | 28(1) | -6(1) | 3(1) | -1(1) |
| O(1) | 28(2) | 21(2) | 41(2) | -6(1) | -12(2) | 1(1) |
| N(1) | 21(2) | 17(2) | 14(2) | 6(2) | 1(2) | 0(1) |
| N(2) | 18(2) | 17(2) | 16(2) | 4(1) | -1(1) | 1(1) |
| N(3) | 26(2) | 18(2) | 14(2) | 0(1) | -1(2) | 4(2) |
| C(1) | 21(2) | 16(2) | 12(2) | -4(2) | 5(2) | -4(2) |
| C(2) | 17(2) | 24(2) | 20(2) | 2(2) | 1(2) | 2(2) |
| C(3) | 16(2) | 24(2) | 18(2) | 2(2) | 2(2) | 2(2) |
| C(4) | 25(2) | 12(2) | 14(2) | 0(2) | -1(2) | 2(2) |
| C(5) | 28(2) | 28(2) | 13(2) | 7(2) | 5(2) | 5(2) |
| C(24) | 32(2) | 32(2) | 15(2) | 5(2) | 3(2) | 11(2) |
| C(23) | 27(2) | 22(2) | 33(3) | 5(2) | 9(2) | -2(2) |
| C(25) | 36(3) | 36(3) | 27(3) | 14(2) | 11(2) | 11(2) |
| C(14) | 15(2) | 20(2) | 19(2) | 7(2) | 3(2) | 0(2) |
| C(19) | 17(2) | 24(2) | 22(2) | 6(2) | 2(2) | 4(2) |
| C(18) | 29(2) | 18(2) | 36(3) | 6(2) | 5(2) | 0(2) |
| C(17) | 29(2) | 27(2) | 26(3) | 8(2) | 8(2) | 1(2) |
| C(16) | 31(2) | 31(3) | 22(3) | -1(2) | 5(2) | 1(2) |
| C(15) | 24(2) | 20(2) | 21(2) | -1(2) | 3(2) | -1(2) |
| C(22) | 34(2) | 23(2) | 26(3) | -1(2) | 2(2) | 3(2) |
| C(21) | 57(3) | 39(3) | 34(3) | 13(2) | 20(3) | -2(3) |
| C(20) | 46(3) | 24(2) | 21(3) | -2(2) | 4(2) | -9(2) |
| C(6) | 26(2) | 25(2) | 22(3) | 10(2) | 3(2) | 7(2) |
| C(11) | 25(2) | 41(3) | 25(3) | 8(2) | 4(2) | 10(2) |
| C(10) | 38(3) | 56(4) | 31(3) | 23(3) | 1(2) | 17(3) |
| C(9) | 39(3) | 43(3) | 56(4) | 30(3) | 21(3) | 21(2) |
| C(8) | 40(3) | 25(2) | 49(4) | 13(2) | 21(3) | 13(2) |
| C(7) | 28(2) | 23(2) | 32(3) | 8(2) | 13(2) | 2(2) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(13) | 48(3) | 58(3) | 24(3) | -4(3) | -7(2) | 9(3) |
| C(12) | 40(3) | 21(2) | 34(3) | 0(2) | 8(2) | -8(2) |
| C(26) | 26(2) | 32(3) | 48(3) | -1(2) | -5(2) | 12(2) |
| C(27) | 46(3) | 53(4) | 74(5) | -6(3) | -29(3) | 18(3) |
| C(28) | 32(3) | 64(4) | 109(6) | -30(4) | -24(3) | 2(3) |
| C(29) | 49(3) | 30(3) | 97(5) | -12(3) | -46(3) | -7(2) |
| C(30) | 92(7) | 73(5) | 67(5) | 13(4) | -6(5) | -1(5) |
| Cl(4) | 77(2) | 121(3) | 62(2) | -13(2) | 3(2) | -9(2) |
| Cl(5) | 145(4) | 75(2) | 107(2) | -27(2) | 1(3) | 7(2) |
| C(30A) | 92(7) | 73(5) | 67(5) | 13(4) | -6(5) | -1(5) |
| Cl(4A) | 77(2) | 121(3) | 62(2) | -13(2) | 3(2) | -9(2) |
| Cl(5A) | 145(4) | 75(2) | 107(2) | -27(2) | 1(3) | 7(2) |

Table 25. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for **6b**.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2) | -528 | 1122 | 1224 | 24 |
| H(3) | -350 | 1524 | -495 | 23 |
| H(6A) | -85 | 999 | 4055 | 40 |
| H(6B) | -529 | 869 | 4144 | 40 |
| H(6C) | -386 | 1128 | 3056 | 40 |
| H(7A) | -625 | 570 | 1521 | 41 |
| H(7B) | -797 | 381 | 2700 | 41 |
| H(7C) | -512 | 136 | 1874 | 41 |
| H(8A) | -48 | -3 | 3419 | 49 |
| H(8B) | -353 | 189 | 4307 | 49 |
| H(8C) | 89 | 328 | 4317 | 49 |
| H(11) | 699 | 2337 | -2114 | 33 |
| H(13) | 707 | 1331 | -3925 | 34 |
| H(15A) | 531 | 2363 | -77 | 41 |
| H(15B) | 523 | 1963 | 638 | 41 |
| H(15C) | 132 | 2134 | 85 | 41 |
| H(16A) | 1162 | 2159 | -4051 | 65 |
| H(16B) | 738 | 2291 | -4453 | 65 |
| H(16C) | 913 | 1889 | -4910 | 65 |
| H(17A) | 548 | 704 | -1848 | 45 |
| H(17B) | 419 | 771 | -3190 | 45 |
| H(17C) | 110 | 817 | -2146 | 45 |
| H(20) | 1144 | -87 | 4962 | 50 |
| H(21) | 1072 | -677 | 4000 | 55 |
| H(22) | 712 | -718 | 2281 | 46 |
| H(24A) | 1120 | 632 | 4824 | 65 |
| H(24B) | 667 | 612 | 5102 | 65 |
| H(24C) | 817 | 828 | 3939 | 65 |
| H(25A) | 364 | -436 | 713 | 47 |
| H(25B) | 373 | 24 | 539 | 47 |

| | | | | |
|---|---|---|---|---|
| H(25C) | 42 | -170 | 1330 | 47 |
| H(26A) | 1735 | 400 | 1228 | 43 |
| H(26B) | 1441 | 163 | 2064 | 43 |
| H(27A) | 1793 | 297 | 3742 | 69 |
| H(27B) | 2139 | 262 | 2787 | 69 |
| H(28A) | 2031 | 904 | 3961 | 82 |
| H(28B) | 2211 | 910 | 2652 | 82 |
| H(29A) | 1506 | 1179 | 3345 | 71 |
| H(29B) | 1709 | 1233 | 2078 | 71 |
| H(30A) | 1782 | 9062 | 5902 | 93 |
| H(30B) | 2241 | 9072 | 5682 | 93 |
| H(30C) | 1759 | 9085 | 6347 | 93 |
| H(30D) | 1594 | 9445 | 5609 | 93 |