Refinement of the crystal structure of dichloro-bis(pyridine-*N*)-copper(II), $C_{10}H_{10}Cl_2CuN_2$, *at 100 K*

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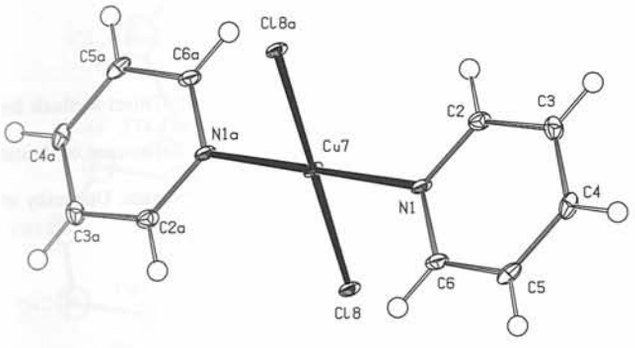

Abstract

$C_{10}H_{10}Cl_2CuN_2$, monoclinic, $P12_1/n1$ (No. 14), $a = 3.7911(2)$ Å, $b = 8.5205(3)$ Å, $c = 16.9910(7)$ Å, $\beta = 91.973(3)°$, $V = 548.5$ Å^3, $Z = 2$, $R_{gt}(F) = 0.033$, $wR_{ref}(F^2) = 0.086$, $T = 100$ K.

Source of material

Crystals of the dichloro-bis(pyridine-*N*)-copper(II) complex were unexpectly formed during an experiment to synthesize lanthanide-containing copper-metallacrowns [1]. Lysine hydroxamic acid hydrochloride, L-LysHa · HCl (2 mmol) was dissolved in 50 mL of water in presence of 2 mmol of $Cu(OAc)_2 \cdot H_2O$. The deep green solution turned blue after adding 0.4 mmol of $La(NO_3)_3 \cdot 6H_2O$. The solvent was partially removed under reduced pressure and pyridine was added as a base. The solution was left to evaporate at room temperature. X-ray diffraction indicated that no crystals of a metallacrown were formed, but that the blue needle-like crystals are of dichloro-bis(pyridine-*N*)-copper(II).

Discussion

The crystal structure of this compound at room temperature was described first by Kabalkina [2] and later by Morosin [3]. The unit cell parameters at 100 K were refined on 3492 reflections and indicate a decrease of the cell volume by 1.8% as compared to room temperature [3]. The low temperature refinement resulted in a more accurate determination of the crystallographic parameters as illustrated for example by the lower $R_{gt}(F)$ value (0.033 compared to 0.052 in [3]) and the lower e.s.d. values.

The average e.s.d. on C—C and C–N bond lengths is 0.0035 Å and 0.0030 Å, respectively (compared to 0.010 Å and 0.008 Å in [3]), the e.s.d. on the Cu—Cl bond length is reduced from 0.002 Å in [3] to 0.0005 Å in this refinement.

The point group of the complex is C_{2h}, with a square planar coordination geometry for Cu and the pyridine rings in *trans* position. These ring makes an angle of 57.45(8)° with the Cu7—Cl8 bond. The packing is dominated by aromatic ring stacking interactions (distance between stacking pyridine rings is 5.903 Å).

Table 1. Data collection and handling.

Crystal:	blue needles, size 0.10 × 0.10 × 0.30 mm
Wavelength:	Cu K_α radiation (1.54178 Å)
μ:	70.01 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 6000 CCD, ω/φ
$2\theta_{max}$:	141.62°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4612, 1042
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1010
$N(param)_{refined}$:	70
Programs:	SHELXS-97 [4], SHELXL-97 [5], PLATON [6]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(2)	4*e*	0.3644	0.0405	0.1689	0.013
H(3)	4*e*	0.3926	0.2302	0.2654	0.015
H(4)	4*e*	0.5781	0.4830	0.2336	0.015
H(5)	4*e*	0.7179	0.5378	0.1039	0.016
H(6)	4*e*	0.6691	0.3418	0.0109	0.013

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Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	4*e*	0.5163(5)	0.1721(2)	0.0809(1)	0.014(1)	0.0042(9)	0.0083(9)	0.0010(7)	–0.0020(8)	0.0008(7)
C(2)	4*e*	0.4350(6)	0.1415(3)	0.1559(1)	0.014(1)	0.007(1)	0.010(1)	–0.0009(8)	–0.0016(9)	0.0000(8)
C(3)	4*e*	0.4526(7)	0.2546(3)	0.2142(1)	0.015(1)	0.013(1)	0.009(1)	0.0001(9)	0.0012(9)	–0.0030(9)
C(4)	4*e*	0.5614(7)	0.4053(3)	0.1952(2)	0.014(1)	0.010(1)	0.013(1)	0.0016(9)	–0.0015(9)	–0.0065(9)
C(5)	4*e*	0.6446(7)	0.4379(3)	0.1181(2)	0.016(1)	0.004(1)	0.019(1)	–0.0004(9)	–0.0003(9)	–0.0012(9)
C(6)	4*e*	0.6166(6)	0.3192(3)	0.0627(1)	0.015(1)	0.006(1)	0.012(1)	0.0004(9)	0.0001(9)	0.0024(9)
Cu(7)	2*b*	1/2	0	0	0.0166(3)	0.0022(3)	0.0061(3)	0.0020(2)	–0.0032(2)	–0.0020(2)
Cl(8)	4*e*	0.1081(1)	0.14445(6)	–0.07764(3)	0.0147(3)	0.0040(3)	0.0086(3)	0.0004(2)	–0.0023(2)	0.0005(2)

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Crystal structure of pentakispiperidyltantal(V), $Ta(NC_5H_{10})_5$

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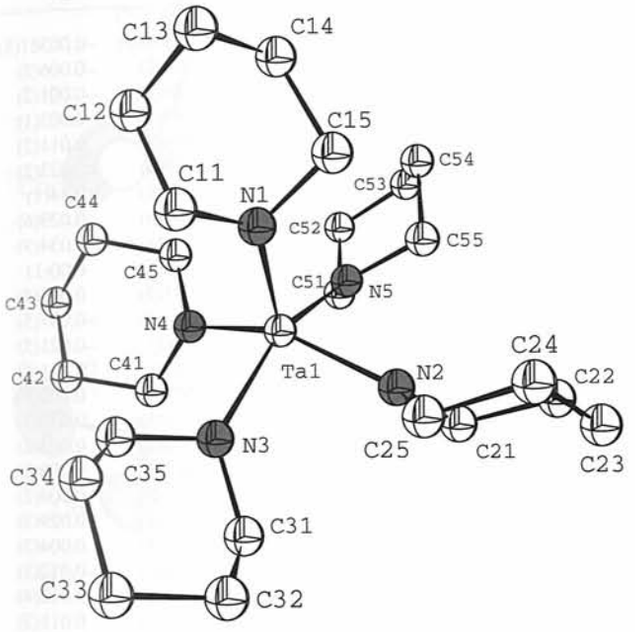

Abstract

$C_{25}H_{50}N_5Ta$, monoclinic, $P12_1/c1$ (No. 14), $a = 15.3542(9)$ Å, $b = 9.9150(6)$ Å, $c = 18.141(1)$ Å, $\beta = 108.109(1)°$, $V = 2624.9$ Å^3, $Z = 4$, $R_{gt}(F) = 0.053$, $wR_{ref}(F^2) = 0.142$, $T = 100$ K.

Source of material

Pentakispiperidyltantal(V) was obtained by reacting tantal pentachloride with lithiated piperidine in hexane [1]. Transparent red crystals were grown from hexane solution at 278 K. The compound is sensitive to air and moisture, so that it is to be handled under dry and oxygen-free argon.

Experimental details

All non-hydrogen atoms were refined anisotropically, hydrogen atoms were calculated isotropically with fixed positions.

Discussion

The coordination sphere of tantalum in $Ta(NC_5H_{10})_5$ is square pyramidal as it has been observed in $Ta[N(CH_3)_2]_5$ [2] and $Nb(NC_5H_{10})_5$ [3,4], the shortest distances are d(Ta—N1) = 197.5(4) pm, d(Ta—N2-5) in the range from 202.3(5) pm to 203.8(5) pm. The piperidine rings are in the common *armchair* conformation. Because of nitrogen-tantalum backbond interactions the nitrogen seeks for a trigonal planar coordination. Bond lengths are in good agreement with literature values [2,4].

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Table 1. Data collection and handling.

Crystal:	red transparent block, size 0.1 × 0.2 × 0.4 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	42.08 cm^{-1}
Diffractometer, scan mode:	Smart APEX (Bruker AXS), ω
$2\theta_{max}$:	70.42°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	40945, 11119
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 9332
$N(param)_{refined}$:	280
Programs:	SHELXS-97 [5], SHELXL-97 [6], DIAMOND [7]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(11A)	4*e*	0.8262	0.7485	–0.1002	0.156
H(11B)	4*e*	0.7620	0.6803	–0.0579	0.156
H(12A)	4*e*	0.9120	0.6363	0.0529	0.110
H(12B)	4*e*	0.8940	0.5392	–0.0198	0.110
H(13A)	4*e*	0.9609	0.7298	–0.0772	0.156
H(13B)	4*e*	1.0335	0.6428	–0.0130	0.156
H(14A)	4*e*	1.0487	0.8556	0.0469	0.201
H(14B)	4*e*	0.9804	0.7805	0.0825	0.201
H(15A)	4*e*	0.9152	1.0048	0.0192	0.078
H(15B)	4*e*	0.9063	0.9357	–0.0616	0.078
H(21A)	4*e*	0.6873	1.2249	0.0589	0.113
H(21B)	4*e*	0.6108	1.2444	–0.0208	0.113
H(22A)	4*e*	0.7045	1.4346	0.0023	0.127
H(22B)	4*e*	0.7923	1.3452	0.0151	0.127
H(23A)	4*e*	0.7561	1.4328	–0.1064	0.129
H(23B)	4*e*	0.6542	1.3836	–0.1262	0.129
H(24A)	4*e*	0.7302	1.2318	–0.1829	0.075
H(24B)	4*e*	0.8081	1.2111	–0.1036	0.075
H(25A)	4*e*	0.6233	1.1298	–0.1327	0.097
H(25B)	4*e*	0.7048	1.0298	–0.1243	0.097
H(31A)	4*e*	0.5346	1.0244	–0.0748	0.033
H(31B)	4*e*	0.4779	0.8979	–0.0651	0.033
H(32A)	4*e*	0.4362	0.9532	–0.1970	0.034
H(32B)	4*e*	0.5388	0.9461	–0.1957	0.034
H(33A)	4*e*	0.4704	0.7465	–0.2488	0.068
H(33B)	4*e*	0.4319	0.7230	–0.1790	0.068
H(34A)	4*e*	0.6199	0.7160	–0.1680	0.106
H(34B)	4*e*	0.5621	0.5897	–0.1594	0.106
H(35A)	4*e*	0.5437	0.6838	–0.0447	0.096
H(35B)	4*e*	0.6481	0.6627	–0.0349	0.096
H(41A)	4*e*	0.5690	0.7792	0.0732	0.078
H(41B)	4*e*	0.6125	0.7909	0.1635	0.078
H(42A)	4*e*	0.5560	0.5713	0.1364	0.096
H(42B)	4*e*	0.6086	0.5513	0.0757	0.096
H(43A)	4*e*	0.6911	0.5658	0.2383	0.142
H(43B)	4*e*	0.6905	0.4382	0.1868	0.142
H(44A)	4*e*	0.7854	0.5414	0.1292	0.144
H(44B)	4*e*	0.8311	0.5508	0.2194	0.144
H(45A)	4*e*	0.7828	0.7747	0.2191	0.164
H(45B)	4*e*	0.8402	0.7609	0.1615	0.164

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(51A)	4*e*	0.7398	0.9827	0.2066	0.072
H(51B)	4*e*	0.7594	1.1374	0.2045	0.072
H(52A)	4*e*	0.8560	1.0468	0.3190	0.074
H(52B)	4*e*	0.8940	0.9410	0.2723	0.074
H(53A)	4*e*	0.9996	1.1145	0.3086	0.204

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(53B)	4*e*	0.9232	1.2223	0.2714	0.204
H(54A)	4*e*	0.9805	1.0194	0.1838	0.298
H(54B)	4*e*	1.0045	1.1733	0.1818	0.298
H(55A)	4*e*	0.8425	1.2231	0.1294	0.236
H(55B)	4*e*	0.833	1.1310	0.0725	0.236

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ta(1)	4*e*	0.72872(1)	0.92399(2)	0.032239(9)	0.01708(8)	0.01652(8)	0.01783(8)	0.00133(5)	0.00358(5)	–0.00361(5)
N(1)	4*e*	0.8256(3)	0.8438(5)	–0.0041(3)	0.029(2)	0.042(3)	0.029(2)	0.013(2)	0.009(2)	–0.006(2)
N(2)	4*e*	0.7016(3)	1.1046(4)	–0.0235(3)	0.020(2)	0.014(2)	0.056(3)	–0.000(1)	–0.006(2)	–0.001(2)
N(3)	4*e*	0.6105(3)	0.8576(4)	–0.0462(2)	0.037(2)	0.014(2)	0.021(2)	–0.004(1)	–0.009(2)	0.002(1)
N(4)	4*e*	0.7059(4)	0.7873(5)	0.1074(3)	0.052(3)	0.028(2)	0.025(2)	–0.018(2)	–0.016(2)	0.011(2)
N(5)	4*e*	0.7998(5)	1.0320(7)	0.1275(3)	0.090(5)	0.065(4)	0.025(2)	–0.056(4)	0.028(3)	–0.023(2)
C(11)	4*e*	0.8201(6)	0.726(1)	–0.0500(8)	0.044(5)	0.15(1)	0.20(2)	–0.030(6)	0.042(7)	–0.14(1)
C(12)	4*e*	0.9026(7)	0.6322(9)	–0.0025(8)	0.117(9)	0.038(4)	0.16(1)	0.033(5)	0.106(9)	0.029(6)
C(13)	4*e*	0.9791(8)	0.699(1)	–0.024(1)	0.107(9)	0.058(6)	0.29(2)	0.041(6)	0.15(1)	0.034(9)
C(14)	4*e*	0.9888(7)	0.814(2)	0.0349(7)	0.051(6)	0.38(3)	0.061(6)	0.10(1)	0.008(5)	0.00(1)
C(15)	4*e*	0.9083(7)	0.9196(9)	–0.0083(7)	0.059(5)	0.053(5)	0.082(7)	0.003(4)	0.021(5)	0.005(4)
C(21)	4*e*	0.6760(7)	1.2305(6)	0.0034(9)	0.070(5)	0.014(2)	0.24(2)	–0.003(3)	0.105(8)	–0.007(5)
C(22)	4*e*	0.7278(8)	1.3528(7)	–0.014(1)	0.115(8)	0.015(3)	0.25(2)	–0.017(4)	0.14(1)	–0.021(5)
C(23)	4*e*	0.7172(5)	1.3615(7)	–0.098(1)	0.032(3)	0.026(3)	0.26(2)	0.004(3)	0.042(6)	0.051(6)
C(24)	4*e*	0.7431(6)	1.2280(7)	–0.1271(5)	0.066(5)	0.035(3)	0.054(4)	–0.024(3)	–0.029(4)	0.022(3)
C(25)	4*e*	0.6878(7)	1.1148(8)	–0.1060(5)	0.090(6)	0.043(4)	0.056(4)	–0.043(4)	–0.053(4)	0.034(3)
C(31)	4*e*	0.5258(3)	0.9287(5)	–0.0857(3)	0.021(2)	0.035(2)	0.022(2)	–0.007(2)	–0.001(2)	0.002(2)
C(32)	4*e*	0.4941(4)	0.9074(5)	–0.1740(3)	0.028(2)	0.027(2)	0.021(2)	–0.005(2)	–0.004(2)	0.002(2)
C(33)	4*e*	0.4830(6)	0.7592(7)	–0.1934(4)	0.075(5)	0.030(3)	0.036(3)	–0.008(3)	–0.027(3)	–0.004(2)
C(34)	4*e*	0.5701(8)	0.6859(8)	–0.1498(5)	0.113(8)	0.032(3)	0.065(5)	0.025(4)	–0.051(5)	–0.029(3)
C(35)	4*e*	0.5938(8)	0.7135(6)	–0.0627(5)	0.116(7)	0.015(2)	0.053(4)	–0.009(3)	–0.054(5)	0.004(2)
C(41)	4*e*	0.6188(8)	0.7480(7)	0.1173(5)	0.127(8)	0.031(3)	0.068(5)	–0.025(4)	0.075(6)	–0.012(3)
C(42)	4*e*	0.6119(9)	0.5931(8)	0.1248(8)	0.126(9)	0.035(4)	0.121(9)	–0.028(5)	0.099(9)	–0.012(4)
C(43)	4*e*	0.693(1)	0.5360(9)	0.1880(6)	0.28(2)	0.032(4)	0.043(4)	–0.023(7)	0.055(8)	0.011(3)
C(44)	4*e*	0.780(1)	0.5814(8)	0.1763(7)	0.16(1)	0.036(4)	0.084(7)	–0.041(5)	–0.083(8)	0.036(4)
C(45)	4*e*	0.783(1)	0.7349(9)	0.1704(7)	0.18(1)	0.039(4)	0.092(7)	–0.044(6)	–0.108(8)	0.037(5)
C(51)	4*e*	0.7848(8)	1.0485(7)	0.2023(4)	0.129(8)	0.029(3)	0.028(3)	0.012(4)	0.033(4)	–0.004(2)
C(52)	4*e*	0.8708(7)	1.0322(9)	0.2713(4)	0.109(7)	0.057(4)	0.026(3)	–0.029(5)	0.030(4)	–0.016(3)
C(53)	4*e*	0.943(1)	1.131(2)	0.2669(5)	0.26(2)	0.20(2)	0.023(3)	–0.20(2)	0.009(7)	–0.015(6)
C(54)	4*e*	0.959(1)	1.110(3)	0.1876(5)	0.22(2)	0.48(4)	0.024(4)	–0.30(2)	0.009(7)	–0.015(9)
C(55)	4*e*	0.866(1)	1.134(2)	0.1230(5)	0.26(2)	0.28(2)	0.022(3)	–0.25(2)	0.011(7)	–0.005(7)

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