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Crystal structure of 1,1'-methylenebis(4-*tert*-butylpyridinium) tetrachloridocobaltate(II) – dichloromethane (1:1), $C_{20}H_{30}Cl_6CoN_2$

Table 1: Data collection and handling.

Crystal:	Blue block
Size:	$0.23 \times 0.15 \times 0.13$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	1.25 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	27.4° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	38536, 5992, 0.042
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4906
$N(\text{param})_{\text{refined}}$:	348
Programs:	Bruker [1], SHELX [2], WinGX/ORTEP [3]

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Abstract

$C_{20}H_{30}Cl_6CoN_2$, orthorhombic, *Pbca* (no. 61), $a = 20.756(1)$ Å, $b = 9.3427(5)$ Å, $c = 27.6827(12)$ Å, $V = 5368.1(5)$ Å³, $Z = 8$, $R_{\text{gt}}(F) = 0.0235$, $wR_{\text{ref}}(F^2) = 0.0593$, $T = 100(2)$ K.

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The asymmetric unit of the crystal structure is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

A mixture of 4-*tert*-butyl pyridine (0.1 mol), dichloromethane (0.05 mol) and $CoCl_2 \cdot 6H_2O$ (0.1 mol) were stirred together under inert atmosphere at room temperature for 48 h. The resulting blue solution was concentrated under reduced pressure. Crystals suitable for X-ray analysis were obtained by layering a concentrated dichloromethane solution of the product with hexane for a period of two weeks.

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Experimental details

All hydrogen atoms were positioned geometrically, allowed to ride on their parent atoms. The C–H_{aromatic} and C–H_{methylene} distances were restrained to 0.950 Å and 0.99 Å, respectively with $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$. The chlorine atoms of dichloromethane are disordered over two positions with 50% site occupancy for each atom. Furthermore, the disorder of the two *tert*-butyl groups was modelled using PART instructions with the major components having 86% and 95% site occupancy.

Comment

N-heterocyclic carbenes (NHCs) have become a very important class of ligands in organometallic chemistry [4]. They have been reported to have diverse applications in coordination chemistry and catalysis [5]. Chelating bis NHC ligands also show better moisture and air stability for metal complexes and have been attracting more attention [6]. The title compound is a side product of our study on NHC complexes. This class of compounds is not only excellent ammonium salts but also building blocks for metal-organic assemblies and supramolecules [6–9]. Dichloromethane induced the bridging of the two *tert*-pyridine groups which is balanced by a tetrachloridocobaltate(II) anion. Six molecules of water from the cobalt salt are eliminated from the reaction.

The asymmetric unit of the title compound consists of a dicationic 1,1'-methylenebis(4-*tert*-butylpyridinium) species, a tetrachloridocobaltate anion and one CH_2Cl_2 molecule.

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Co1	0.12253(2)	0.47316(2)	0.21473(2)	0.01738(6)
Cl1	0.05284(2)	0.65207(3)	0.23367(2)	0.02007(8)
Cl2	0.13971(2)	0.34964(4)	0.28474(2)	0.02072(8)
Cl3	0.21464(2)	0.56612(4)	0.18182(2)	0.02806(10)
Cl4	0.07349(2)	0.32487(4)	0.16045(2)	0.02286(9)
N1	0.09101(6)	0.96506(12)	0.18495(4)	0.0167(3)
N2	0.12900(6)	0.96045(12)	0.26795(4)	0.0176(3)
C1A ^a	0.15891(9)	0.82126(18)	0.43923(6)	0.0302(4)
H1AA ^a	0.184724	0.908493	0.435804	0.045 [*]
H1AB ^a	0.170402	0.772846	0.469433	0.045 [*]
H1AC ^a	0.113069	0.846368	0.439795	0.045 [*]
C2A ^a	0.24337(10)	0.6761(2)	0.39858(7)	0.0460(6)
H2AA ^a	0.252445	0.608284	0.372431	0.069 [*]
H2AB ^a	0.252218	0.630423	0.429755	0.069 [*]
H2AC ^a	0.270822	0.760716	0.394916	0.069 [*]
C3A ^a	0.12905(10)	0.5897(2)	0.40035(7)	0.0394(5)
H3AA ^a	0.083856	0.619891	0.401373	0.059 [*]
H3AB ^a	0.139557	0.537011	0.429928	0.059 [*]
H3AC ^a	0.135981	0.527736	0.372266	0.059 [*]
C1B ^b	0.2048(12)	0.822(2)	0.4310(9)	0.021(4)
H1BA ^b	0.245898	0.853789	0.417252	0.031 [*]
H1BB ^b	0.212713	0.772862	0.461715	0.031 [*]
H1BC ^b	0.177034	0.905237	0.436606	0.031 [*]
C2B ^b	0.2136(12)	0.590(2)	0.3850(10)	0.025(4)
H2BA ^b	0.190653	0.528234	0.362061	0.037 [*]
H2BB ^b	0.222005	0.536533	0.414801	0.037 [*]
H2BC ^b	0.254500	0.620746	0.370749	0.037 [*]
C3B ^b	0.1088(9)	0.669(3)	0.4203(10)	0.025(4)
H3BA ^b	0.092723	0.742927	0.442391	0.038 [*]
H3BB ^b	0.117003	0.580780	0.438401	0.038 [*]
H3BC ^b	0.076503	0.650654	0.395229	0.038 [*]
C4	0.17225(8)	0.72116(16)	0.39644(5)	0.0233(3)
C5	0.15653(7)	0.80096(15)	0.34979(5)	0.0186(3)
C6	0.09549(7)	0.85665(16)	0.34129(5)	0.0223(3)
H6	0.062172	0.839594	0.364104	0.027 [*]
C7	0.08230(7)	0.93522(16)	0.30096(5)	0.0218(3)
H7	0.040202	0.972335	0.296032	0.026 [*]
C8	0.18791(7)	0.90392(18)	0.27391(6)	0.0280(4)
H8	0.220064	0.919450	0.250061	0.034 [*]
C9	0.20218(8)	0.82401(18)	0.31405(6)	0.0303(4)
H9	0.243980	0.783811	0.317422	0.036 [*]
C10	0.11514(8)	1.05150(15)	0.22549(5)	0.0217(3)
H10A	0.082580	1.124421	0.234287	0.026 [*]
H10B	0.154914	1.101993	0.215534	0.026 [*]
C11	0.02741(7)	0.95258(15)	0.17775(5)	0.0211(3)
H11	−0.001629	1.000606	0.198746	0.025 [*]
C12	0.00375(7)	0.87176(16)	0.14064(5)	0.0225(3)
H12	−0.041511	0.863510	0.136355	0.027 [*]
C13	0.04510(8)	0.80153(15)	0.10912(5)	0.0201(3)
C14	0.11068(8)	0.81667(17)	0.11796(6)	0.0281(4)
H14	0.140660	0.769719	0.097436	0.034 [*]
C15	0.13291(7)	0.89740(17)	0.15544(6)	0.0256(4)
H15	0.177952	0.906073	0.160803	0.031 [*]
C16	0.01979(8)	0.71576(16)	0.06613(5)	0.0265(4)
C17A ^c	−0.05205(17)	0.6717(4)	0.07369(9)	0.0435(10)

Table 2 (continued)

Atom	x	y	z	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
H17A ^c	−0.055927	0.614929	0.103314	0.065 [*]
H17B ^c	−0.066598	0.614608	0.046061	0.065 [*]
H17C ^c	−0.078724	0.757857	0.076426	0.065 [*]
C18A ^c	0.0601(2)	0.5836(3)	0.05691(11)	0.0445(9)
H18A ^c	0.103980	0.612150	0.048201	0.067 [*]
H18B ^c	0.041049	0.528443	0.030381	0.067 [*]
H18C ^c	0.061221	0.524598	0.086163	0.067 [*]
C19A ^c	0.02190(18)	0.8150(4)	0.02210(12)	0.0274(7)
H19A ^c	−0.003921	0.900678	0.028565	0.041 [*]
H19B ^c	0.004377	0.764800	−0.006081	0.041 [*]
H19C ^c	0.066585	0.842906	0.015635	0.041 [*]
C17B ^d	−0.0284(7)	0.6136(15)	0.0840(5)	0.022(3)
H17D ^d	−0.008680	0.551474	0.108437	0.033 [*]
H17E ^d	−0.044203	0.555188	0.057144	0.033 [*]
H17F ^d	−0.064449	0.666046	0.098518	0.033 [*]
C18B ^d	0.0803(7)	0.6157(18)	0.0507(8)	0.033(4)
H18D ^d	0.116543	0.676435	0.040943	0.050 [*]
H18E ^d	0.067744	0.554094	0.023667	0.050 [*]
H18F ^d	0.093190	0.556261	0.078232	0.050 [*]
C19B ^d	0.0060(11)	0.819(2)	0.0267(8)	0.024(4)
H19D ^d	0.043304	0.881693	0.021995	0.037 [*]
H19E ^d	−0.031696	0.876805	0.035301	0.037 [*]
H19F ^d	−0.002777	0.766534	−0.003258	0.037 [*]
C20	0.30470(9)	0.7582(2)	0.07661(6)	0.0475(5)
H20A	0.327626	0.806474	0.103412	0.057 [*]
H20B	0.274963	0.687300	0.091054	0.057 [*]
Cl5A ^d	0.2598(3)	0.8840(6)	0.04592(16)	0.0665(14)
Cl6A ^d	0.3603(3)	0.6687(4)	0.04183(19)	0.0550(7)
Cl5B ^d	0.2553(2)	0.8902(5)	0.04699(11)	0.0360(7)
Cl6B ^d	0.3527(3)	0.6712(6)	0.02990(19)	0.0798(15)

^aOccupancy: 0.949(2), ^bOccupancy: 0.051(2), ^cOccupancy: 0.858(8), ^dOccupancy: 0.142(8), ^eOccupancy: 0.5.

The anionic cobalt(II) complex has a slightly distorted tetrahedral geometry with Co—Cl bond distances lying between 2.2716(5) and 2.2888(5) Å and Cl—Co—Cl bond angles ranging from 105.98(2) to 113.52(2)°. These bond parameters around the metal centre are comparable to those of similar compounds in literature [6–9]. The 1,1'-methylenebis(4-*tert*-butylpyridinium) cation has a V-shape conformation, which is defined by the bridging —CH₂— group. Furthermore, the dihedral angle between the two pyridinium rings was found to be 67.9°. Intermolecular Co(1)—Cl(1)···C(7) and Co(1)—Cl(1)···C(11) halogen bonds were observed with Cl···C contact distances of 3.293(2) and 3.249(1) Å, respectively. The shortened Cl···C contact could be engendered by the Coulombic attraction (positively charged nitrogen atoms N1 and N2) between the 1,1'-methylenebis(4-*tert*-butylpyridinium) and [CoCl₄]^{2−} anion.

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