[Tetraphenylphosphonium](1+) \{3,3'-comno-bis-[\eta^5-1,2-dicarba-(3)-nickel(III)-closo-dodecaborate]\}(1–)-monotetrachloromethanate, \[\{(\text{C}_6\text{H}_5)_4\text{P}\}^+\{\text{Ni}^{3+}\{\eta^5-(3)-1,2-\text{B}_9\text{C}_2\text{H}_{11}\}_2\}^- \cdot \text{CCl}_4\]: Synthesis, Structure, and Temperature-Dependent EPR Spectra

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Received July 18, 2007

Abstract—A novel compound containing tetraphenylphosphonium and nickel dicarbolyl, \([\text{P(C}_6\text{H}_5)_3\text{Ni}](\text{Ni}^+\text{B}_9\text{C}_2\text{H}_{11})_2 \cdot \text{CCl}_4\) (I) was synthesized and studied by X-ray diffraction and EPR methods. The crystals are monoclinic: \(\text{C}_2\text{H}_5\text{NiB}_9\text{C}_2\text{H}_{11}\) \((M = 816.69)\), space group \(P2_1/c\), the unit cell parameters \(a = 13.3964(5), b = 7.0556(2), c = 20.6610(8) \, \text{Å}\), \(\beta = 94.9070(13)°\), \(V = 1945.7(2) \, \text{Å}^3\), \(Z = 2\), \(\rho(\text{calcld.}) = 1.394 \, \text{g/cm}^3\), \(T = 100 \, \text{K}\), \(F(000) = 834, \mu = 0.081 \, \text{mm}^{-1}\). The structure was solved by the direct and Fourier methods and refined by the full-matrix least-squares method in the anisotropic (isotropic for the hydrogen atoms) approximation \((R_1 = 0.032\) for 4027 \(I_{\text{obs}} \geq 2\sigma(I)), 19886\) measured and 5379 independent \(I_{\text{obs}}\). \(\chi_8\) APEX Bruker diffractometer, \(\lambda\text{MoK}_\alpha\), graphite monochromator, \(\phi/\omega\) scan mode). At 100 K, the crystal contains the intermolecular hydrogen bonds B–H–C–Cl that favor the formation of infinite chains of the alternating anions and solvate molecules along the \(z\) axis of the unit cell. The single-crystal EPR study of complex I showed that the temperature changes of the cell parameters induce changes in the parameter of the \(g\)-factor \(g_3\) directed along \(\text{C}_2\text{B}–\text{Ni}–\text{C}_2\text{B}\). The cell parameters are increased and the \(g_3\) value is gradually decreased with the increasing temperature. The temperature study of the EPR spectra of the powdered compound I revealed also jumpwise changes in \(g_2\) and \(g_3\) with hysteresis at 183–203 K depending on the direction of the temperature changes. The differences observed in the EPR spectra of the powders and single crystal of compound I in both the \(g\)-factor and the temperature dependence of its components are supposed to be caused by the \(\text{CCl}_4\) vacancies formed in the crystal structure of a complex as a result of the partial removal of the solvate \(\text{CCl}_4\) molecules when grinding the sample and by the change in the liability of the solvate molecules of a solvent with temperature.

DOI: 10.1134/S1070328408090078

The atoms, molecules, and ions are known to be involved in the complex interactions in compounds containing the hydrocarbon and hydride hydrogen atoms, the planar, cyclic, three-dimensional cluster aromatic (and even hyperaromatic) components, as well as the paramagnetic atoms are [1–4]. The above interactions change the structural, electronic, spectral, and the other physical properties of compounds. The title compound, \(\{(\text{C}_6\text{H}_5)_4\text{P}\}^+\{\text{Ni}^{3+}\{\eta^5-(3)-1,2-\text{B}_9\text{C}_2\text{H}_{11}\}_2\}^- \cdot \text{CCl}_4\) (I), which is the paramagnetic salt-like metal derivative of ortho-carborane(12), exhibits the above—mentioned complex interactions. The complex anion [NiCbl] has a sandwich structure with the Ni(II) atoms coupled with two cluster ligands B_9C_2H_11^- (Cb), which have a three-dimensional aromaticity [3, 4]. The paramagnetic Ni(III) atom has the 3d^8 electronic configuration with \(S = 1/2\) and realizes hypothetical C.N. 10. This configuration interacts with the electrons of two Cb ligands delocalized over the cluster atoms and enters their aromatic structure. Such systems with the delocalized electrons and hydride H atoms can interact with the planar benzoid aromatic fragments Ph of the [Ph_2P] cation, which should be followed by the structural and EPR changes of a complex.

This paper reports the synthesis, single-crystal X-ray diffraction and EPR study of the powder and single crystal of a novel complex I. One of the tasks of this work was to establish the reason for the temperature changes in the \(g\)-factor observed for the (NiCbl)_2 complex with different cations.

EXPERIMENTAL

Synthesis. The title compound I was synthesized as described in [4] by the precipitation of a bulky anion in
aqueous media (pH ≈ 4.5) with the [Ph₄P]+ cation according to the reaction

\[
\text{Cs[NiCl₂]} + [\text{Ph₄P}]\text{Br} = [\text{Ph₄P}][\text{NiCl₂}] \downarrow + \text{CsBr}
\]

with subsequent filtration, drying, and recrystallization of the target product. The starting compound II was synthesized and identified by the known procedures [4, 5]. A weighed sample of compound III of the pure grade (0.184 g, 0.44 mmol) was dissolved in 200 ml of water at 70°C. Compound II (0.201 g, 0.44 mmol) was dissolved in 400 ml of hot water (70°C). Then, 50 ml of the acetate buffer solution (pH 4.56) and 0.05 g of Na₂SO₄ (to suppress the Ni³⁺ oxidation) were added. In air, compound II is gradually oxidized in a solution to [Ni⁴⁺Cl₂]⁰ insoluble in water. To remove the latter, the above solution of compound II was filtered and immediately poured to the stirred solution of III at 70°C. The light brown amorphous precipitate of [Ph₄P][NiCl₂] (IV) that formed was coagulated by the addition of CaCl₂. On cooling, the precipitate of IV was filtered, washed with water on the filter, dried in air, and in vacuum at room temperature to a constant weight. The yield of amorphous compound IV was 0.260 g (0.39 mmol, 89% as compared to II). Compound IV is soluble in acetone, acetonitrile, benzene, DMF, DMSO, THF; CHCl₃, CH₂Cl₂, insoluble in CCl₄.

Crystals of I suitable for X-ray diffraction study were obtained by crystallization of IV dissolved in a mixture CH₃Cl₂–CCl₄, on slow fractional evaporation at room temperature of a low-boiling methane molecules CCl₄. The cation has common geometry. The P atom has a tetrahedral arrangement. The P atom has a tetrahedral arrangement. The C–C, C–H bond lengths and bond angles in the anion are presented in Table 3. The anisotropic thermal parameters, the coordinates of the hydrogen atoms, and tables of the structural factors are available from the authors.

The EPR spectra were recorded on a E-109 Varian automated spectrometer in the X-range of frequencies at 77–300 K and were modeled and analyzed with the WinEPR and Simfonia programs.

### RESULTS AND DISCUSSION

Compound I occurs as brown crystals. Its crystal structure is built of the tetrakisphosphonium cations (PPh₄)⁺ (on axes 2), the centrosymmetric nickel dicarbonyl anions Ni(C₅H₇)²⁻, and the solvate tetrachloromethane molecules CCl₄ (on axes 2) in a ratio 1 : 1 : 1.

The structure of the [Ni(B₆C₅H₁₁)₂]⁺ anion in I with atomic numbering is shown in Fig. 1.

The cation has common geometry. The P atom has a distorted tetrahedral coordination (P–C 1.794(2) Å, the CPC angles 106.2(1)°–111.2(1)°). The C–C, C–H bond lengths and CCC angles in the phenyl rings lie in the intervals 1.379(3)–1.404(3), 0.86(2)–0.94(3) Å and 119.5(2)°–120.4(2)°, respectively. The phenyl rings are planar ±0.003–0.005 Å).

The anion has the form of two icosahedra with a shared vertex, i.e., the Ni(III) atom. In the anions, two planes {C₆B₅} are bonded with the Ni atom according to the η⁵-type and determine the conventional pentago-