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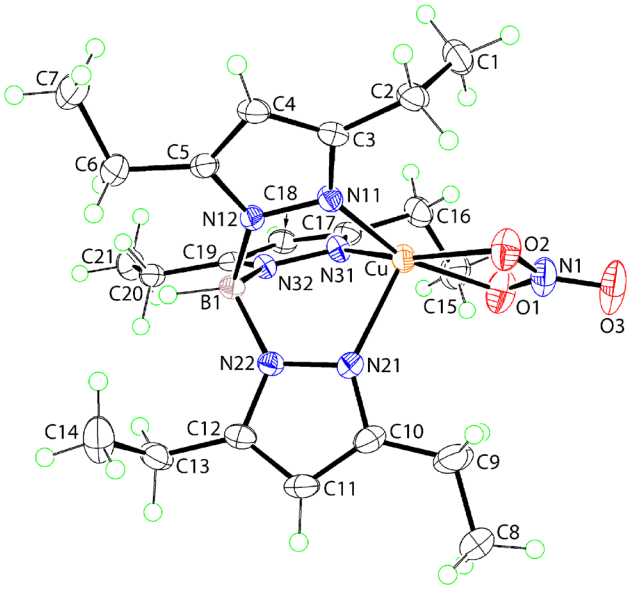
Crystal structure of nitrato-κ^2O,O'-[hydridotris(3,5-diethylpyrazol-1-yl)borato-κ^3N,N',N'']copper(II), $C_{21}H_{34}BCuN_7O_3$



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Abstract

$C_{21}H_{34}BCuN_7O_3$, monoclinic, $P2_1/c$ (no. 14), a = 8.6529(2) Å, b = 13.8775(4) Å, c = 20.3673(6) Å, β = 96.077(3)°, V = 2431.97(12) Å^3, Z = 4, $R_{gt}(F)$ = 0.0377, $wR_{ref}(F^2)$ = 0.1012, T = 178 K.

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The molecular structure is shown in the figure; only the major component of the disorderd ethyl group is illustrated. Table 1 contains the crystallographic data and the list of the atoms including atomic coordinates and displacement parameters can be found in the cif-file attached to this article.

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1 Source of material

Potassium hydridotris(3,5-diethylpyrazol-1-yl)borate (denoted as KL) was obtained by the reaction of KBH_4 with 3.3 equiv. of 3,5-diethylpyrazole.[5] A solution of KBH_4 (117 mg, 0.348 mmol) in CH_2Cl_2 (10 mL) was added to a solution of $Cu(NO_3)_2{\cdot}3H_2O$ (75.0 mg, 0.310 mmol) in CH_3OH (15 mL). After stirring for 30 min at room temperature, the solvent was evaporated under reduced pressure to afford a green powder. The resulting solid was extracted with CH_2Cl_2 (25 mL) to separate any residual salts. The solvent was evaporated under reduced pressure again to afford a green powder (132 mg, 0.260 mmol, 84 % yield). Crystals suitable for X-ray crystallography were obtained by the slow evaporation of a saturated CH_2Cl_2/CH_3OH (1:1 v/v) solution held at room temperature (40.7 mg, 0.080 mmol, 26 % yield). **Anal. Calcd.** for $C_{21}H_{34}BCuN_7O_3$ 1/4(H_2O); bulk material: C, 49.32; H, 6.80; N, 19.17. Found: C, 49.24; H, 6.81; N, 19.10. **IR** (KBr, cm^{-1}): 2972s ν(C–H), 2935s ν(C–H), 2877m ν(C–H), 2545m ν(B–H), 1550s $\nu_{asym}(NO_3)$, 1441s, 1399s, 1384s, 1311s, 1239s $\nu_{sym}(NO_3)$, 1173s, 1045s, 1239s, 1011s ν(N=O), 803s, 638m, 505w ν(Cu–Npz). **Far-IR** (CsI, cm^{-1}): 639s, 505m ν(Cu–Npz), 399m, 321s ν(Cu–NO_3), 288m. **UV–vis** (CH_2Cl_2, λ_{max}, nm (ε, M^{-1} cm^{-1})): 291 (1970), 365 (360), 767 (140). **ESR** ($C_6H_5CH_3$, 130 K): $g_{\parallel}$ = 2.30 ($A_{\parallel}$ 13.9 mT), $g_{\perp}$ = 2.07.

2 Experimental details

The B- and C-bound H atoms were geometrically placed (B–H = 1.12 Å and C–H = 0.95–0.98 Å) and refined as riding with U_{iso}(H) = 1.2–1.5U_{eq}(B, C). The C8, C9-ethyl group was disordered over two sites. Each component was refined independently with anisotropic displacement parameters. The major component had a site occupancy factor = 0.590(8).

3 Discussion

Hydridotris(pyrazolyl)borate ligands have been explored in inorganic, organometallic and coordination chemistry

Table 1: Data collection and handling.

Crystal:	Green block
Size:	0.22 × 0.16 × 0.08 mm
Wavelength:	Mo*K*α radiation (0.71073 Å)
μ:	0.94 mm^{-1}
Diffractometer, scan mode:	Rigaku XtaLAB P200, ω scan
θ_{max}, completeness:	26.4°, 100 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	24347, 4966, 0.042
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 4,363
$N(param)_{refined}$:	324
Programs:	Rigaku[1], Il Milione[2], Shelx[3], WinGX[4]

because these anionic ligands can adopt versatile coordination modes and are useful precursors for the preparation of other complexes involving metals from all parts of the Periodic Table.[6] In our previous work in this area, the nitrate anion exhibits both unidentate and bidentate coordination modes.[7,8] Therefore, the structural observations of copper(II) nitrato complexes as well as their IR spectroscopic measurements may provide a good indication as to the structural effects of different hydridotris(pyrazolyl)borate ligands.[7] We describe herein a mononuclear, five-coordinate nitrato copper(II) complex $[Cu(NO_3)(L)]$ with the hindered ligand, hydridotris(3,5-diethylpyrazol-1-yl)borate anion viz. $[L]^-$.[5] The reaction of $CuCl_2{\cdot}3H_2O$ with a slight excess of the potassium salt of $[L]^-$ led to the isolation of the title complex, $[Cu(NO_3)(L)]$, as a green solid.

The IR spectrum of $[Cu(NO_3)(L)]$ exhibited three strong characteristic absorption bands at 1550, 1239 and 1011 cm^{-1} which are assignable to $\nu_{asym}(NO_2)$, $\nu_{sym}(NO_2)$ and ν(N=O), respectively. These bands were also observed in a similar copper(II) nitrato $[Cu(NO_3)(L^1)]$ complex, i.e. at 1545, 1245 and 1015 cm^{-1}, where $[L^1]^-$ is the hydridotris(3,5-diisopropylpyrazol-1-yl)borate anion.[8] The separations in the $\nu_{asym}(NO_2)$ and $\nu_{sym}(NO_2)$ bands, i.e. $\Delta = [\nu_{asym}(NO_2) - \nu_{sym}(NO_2)]$, are 311 cm^{-1} for $[Cu(NO_3)(L)]$ and 300 cm^{-1} for $[Cu(NO_3)(L^1)]$, indicating chelate binding modes.[8] In far-IR region, the broad and strong band at 321 cm^{-1} is assigned to $\nu(Cu–NO_3)$. This assignment was confirmed by the presence of the same broad and strong band at 316 cm^{-1} for $[Cu(NO_3)(L^1)]$.[8]

The molecular structure of $[Cu(NO_3)(L)]$, (I), is illustrated in the figure (50 % displacement ellipsoids). The copper(II) centre is coordinated by a tridentate pyrazoylate ligand and simultaneously chelated by a nitrate anion. The pentacoordinated geometry is based on a square-pyramid. This is quantified by the value of $\tau_5 = 0.05$ which compares to $\tau_5 = 0.0$ for an ideal square-pyramid and $\tau_5 = 1.0$ for an ideal trigonal bipyramid.[9] In this description, the N21 atom occupies the apical position above the square-plane defined by the O1, O2, N11 and N31 atoms [r.m.s. deviation = 0.0317 Å] with the maximum deviation of 0.0359(10) Å being for atom O1; the copper(II) atom lies 0.2639(9) Å above the plane in the direction of the N21 atom. The two Cu–O (nitrate) bond lengths are similar, at 2.0218(17) and 2.0550(16) Å. The Δd(Cu–O) is 0.033 Å, showing an almost symmetric bidentate coordination mode. The equivalent value for $[Cu(NO_3)(L^1)]$ is 0.032 Å, indicating the bulkiness of the ethyl substituents in L^- is the same as that of the isopropyl substitution of L^{1-}.

The similarity in the structures was also confirmed by the d–d transition energy and ESR parameters. In the UV–vis spectrum, the d–d transition energy of the five-coordinate, distorted square-pyramidal geometry for (I) was observed at 767 nm. Moreover, an additional band at 291 nm can be assigned to NO_3^- to the Cu(II) charge transfer band. These bands were also observed for $[Cu(NO_3)(L^1)]$, i.e. at 773 and 293 nm, respectively.[8] The ESR parameters for (I) are $g_{\|} = 2.30$, ($A_{\|} = 13.9$ mT), $g_{\perp} = 2.07$, consistent with a d_{x2-y2} ground state. These data are also consistent with those found for $[Cu(NO_3)(L^1)]$: $g_{\|} = 2.31$, ($A_{\|} = 14.6$ mT), $g_{\perp} = 2.08$.

There is a disparity in the Cu–N (pyrazolyl) bond lengths which covers a relatively broad range, i.e. Cu–N11 [1.9514(16) Å] is clearly the shorter bond followed by Cu–N31 [1.9816(17) Å] which, again, is significantly shorter than Cu–N21 [2.1341(17) Å]. While these deviations suggest a deviation from a putative 3-fold axis, there are also measurable deviations in relevant dihedral angles. Thus, the dihedral angle between the N11-pyrazolyl five-membered ring and those containing the N21 [55.25(7)]° and N31 [62.11(7)]° atoms; the dihedral angle between the N21- and N31-pyrazolyl rings is 62.67(8)°. The distance the copper(II) centre lies out of the three least-squares planes through the N11-, N21- and N31-pyrazolyl rings also varies, 0.168(3), 0.224(3) and 0.103(3) Å, respectively.

In the crystal, there appear to be two significant, directional intermolecular interactions within the three-dimensional architecture. The first of these is a methyl C–H···O (nitrate, non-coordinating) contact [C21–H21a···O3^{i}: H21a···O3^{i} = 2.58 Å, C21···O3^{i} = 3.502(3) Å with angle subtended at the H21a atom = 157° for symmetry operation (i) 1 + *x*, 1/2 − *y*, 1/2 + *z*] which occurs within chains of molecules along the [1 0 3] direction. The second contact occurs between methylene–C–H and a pyrazolyl ring [C13–H13a···Cg(N31, N32, C17–C19)^{ii}: H13a···Cg(N31, N32, C17–C19)^{ii} = 2.99 Å with angle at H13a = 162° for (ii) 1 − *x*, 1/2 + *y*, 3/2 − *z*]. These latter interactions occur between molecules aligned along the *b*-axis.

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