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Synthesis and Molecular Structure of Bis(2,6-dimethylpyridine)bis-(trifluoroacetate)Cr(II) with an Unusual Square Planar Environment of the Chromium Atom

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Earlier we have described a convenient 'boron hydride' synthesis of the dimeric Cr(II) carboxylate adducts [1]:

$$\mathrm{CrCl_3} \xrightarrow[\mathrm{THF}]{\mathrm{NaBH_4}} \{\mathrm{THF\cdot Cr(BH_4)_2}\} \xrightarrow{\mathrm{RCOOH}}$$

$$[\mathrm{THF\cdot CR(OOCR)_2}]_2 \xrightarrow{\mathrm{L}} [\mathrm{L\cdot Cr(OOCR)_2}]_2$$

Analogously to the complexes reported in [2, 3] these dimers have 'lantern' structure with THF, pyridine, γ-picoline, as well as α-substituted pyridines such as α-picoline, quinoline and quinaldine (R = $\mathrm{CMe_3}$) employed as axial L ligands [1]. It should be pointed out that the dimer formation is facilitated by the electron releasing R substituents and bulky L ligands whereas an octahedral monomer $\mathrm{Py_4Cr(OOCMe)_2}$ was obtained with R = Me and L = Py [4]. It seemed interesting to elucidate a result of combination of the strong electron attractive trifluoroacetate groups (R = $\mathrm{CF_3}$) and the bulky 2,6-dimethylpyridine ligands (L$'$). The reaction of $\{\mathrm{THF\cdot Cr(BH_4)_2}\}$ complex [1] with $\mathrm{CF_3COOH}$ followed by addition of L$'$ gave the monomeric complex I:

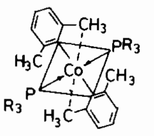
$$\{\mathrm{THF\cdot Cr(BH_4)_2}\} \xrightarrow{\mathrm{CF_3COOH}}$$

$$\{[\mathrm{THF\cdot Cr(OOCCF_3)_2}]_2\} \xrightarrow{\mathrm{2Me_2C_5H_3N}}$$

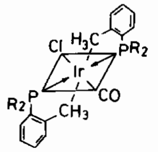
$$(\mathrm{Me_2C_5H_3N})_2\mathrm{Cr(OOCCF_3)_2} \qquad \text{(I)}$$

The violet-red prisms of I obtained by crystallization from a benzene–heptane (3:1) mixture in an ampoule sealed under vacuum are highly sensitive to air oxygen which makes trouble-some their elemental analysis and magnetic measurements. Thus, for reliable elucidation of the structure of I we carried out an X-ray structural analysis of the complex. The monomeric molecule of I (Fig. 1) was found to be in a crystallographic symmetry point coincident with the Cr atom coordinates. The Cr atom has a square planar coordination and is surrounded by two N atoms (Cr–N 2.111(3) Å), two lutidine molecules and two O atoms (Cr–O 2.028(3) Å) of two terminal trifluoroacetate groups. The second O atom in $\mathrm{CF_3}$-COO group is not combined with the Cr atom (Cr$\cdots$O(2) 2.976(3) Å). The CrO(1)C(1)O(2) fragment is planar. It should be stressed that complex I is the first example of Cr(II) with a square-planar environment. In the lutidine ligand the methyl groups are above and under the plane thus blocking the two vacant axial sites in the Cr coordination sphere. Such methyl group orientation in complex I may be a hindrance to a subsequent addition of lutidine molecules.

Analogous behaviour was observed for the bulky ligands with the *ortho*-positioned methyl groups towards the metal-combined atom in the bis(*ortho*-xylene) complex, $\mathrm{(R_3P)_2Co(C_6H_3Me_2)_2}$ (II), [5] and in the *ortho*-tolyl-phosphine complex, *trans*-$\mathrm{(R_3P)_2IrCl(CO)}$, (III) [6] having the square-planar structure:



(II)



(III)

The complexes of type (III) combine readily with an axial ligand Q (CO, $\mathrm{N_2}$ etc.) when R = *p*- and *m*-tolyl (cone angle θ is 145° for $\mathrm{PR_3}$ [7]) but do not react with Q when R = *ortho*-tolyl (θ = 194° for $\mathrm{PR_3}$) in spite of their close electronic effects.

Analogously to the complexes II and III there is no $\mathrm{H_{Me}}$–Cr bonding in I since its shortest distance was 2.845(6) Å (the hydrogen atoms were elucidated from the Fourier difference series).

Experimental

All operations were performed under argon stream. Tetrahydrofuran was dried by distilling over sodium benzophenoneketylate under argon stream. Benzene, heptane and lutidine were distilled over sodium suspension under argon stream. The IR spectra were taken on a UR-20 instrument in KBr

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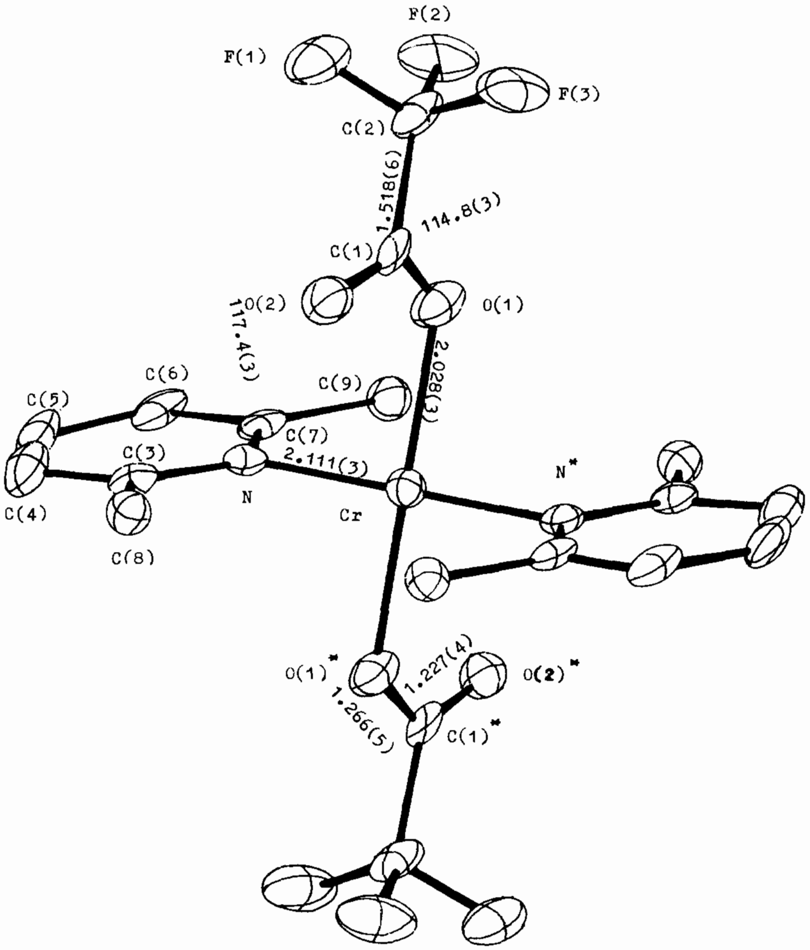

Fig. 1. Structure of the complex.

pellets. The structural analysis was performed on a 'Syntex P2$_\text{I}$' autodiffractometer (MoKα, $2\theta \leqslant 50°$) at -120 °C (the crystal was sealed in a capillary under vacuum). 1200 reflections were detected from which 1081 were involved in a full-matrix iteration. Cell parameters: $a = 8.847(4)$ Å, $b = 9.317(5)$ Å, $c = 12.630(4)$ Å, $\beta = 102.90(4)°$, $V = 1071.9(8)$ Å^3, $Z = 2$, $\rho_\text{calc} = 1.33$, $\rho_\text{found} = 1.35$, R = 4.94%, Rw = 4.55%, spatial group P21/n.

$(Me_2C_5H_3N)_2Cr(OOCCF_3)_2$

A mixture of 1.8 g of $CrCl_3$ and 8 g of $NaBH_4$ in 100 ml of THF was stirred with magnetic stirrer for 2 h and the solution became blue. The solvent was evaporated at 60°/10 torr to dryness, the residue extracted with benzene (70–80 ml) at room temperature to obtain a colourless extract. The extract was concentrated to 40 ml at 60°/10 torr and the solution was titrated with 2 ml of $HOOCCF_3$ in 20 ml of benzene (up to completion of gas evolution). 0.95 g of $Me_2C_5H_3N$ was added to the obtained violet solution. The solution was stored at 5 °C for 24 h and a violet tarry solid precipitated from the violet-red solution. The solution was filtered, diluted with 1/3 volume part of heptane, concentrated to 10–15 ml and transferred to an ampoule at 5°/10 torr. The violet-red prisms precipitated after 7–10 days were separated from the solution, washed with pentane and dried under vacuum. The product was hihgly sensitive to air. Yield 0.25 g. IR spectrum, ν, cm^{-1}: 520w, 560w, 734m, 803m, 970w, 1070m, 1160s, 1220vs, 1460m, 1725s, 2980w, 3140w.

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