Dimeric Fluoro-bridged Five-co-ordinate Cobalt(II)–Pyrazole Complexes; the *X*-Ray Structure of μ-Difluoro-hexakis-(3,5-dimethylpyrazole)-dicobalt(II) Tetrafluoroborate

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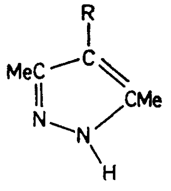
Summary The synthesis and structure of a new class of dinuclear fluoro-bridged five-co-ordinate cobalt(II) complexes and the *X*-ray structure of one of these, μ-difluoro-hexakis-(3,5-dimethylpyrazole)dicobalt(II) tetrafluoroborate are reported.

Reaction of $[Co(H_2O)_6][BF_4]_2$ with an excess of 3,5-dimethylpyrazole (I; R = H), or its 4-substituted derivatives (R = Me, Et, Pr^n, or $PhCH_2$), in anhydrous ethanol–triethyl orthoformate slowly produces violet crystals, which analyse as $Co(ligand)_3BF_5$.† A crystal structure determination for the compound with R = H has been carried out; *crystal data*: *M* = 904·8; *a* = 10·325(5), *b* = 13·753(5), *c* = 17·234(6) Å, β = 117·92(5)°; *Z* = 2, space group: $P2_1/c$. 3084 Reflections were measured using Mo-K_α radiation; least-squares refinement reduced the conventional *R* factor to 0·056.



(I) R = H, Me, Et, Pr^n, or $PhCH_2$

The unit cell contains two dinuclear centrosymmetric dications $[(ligand)_3CoF_2Co(ligand)_3]^{2+}$ (see Figure) and four BF_4^- counter ions. These compounds appear to be the first series of transition-metal complexes containing a structurally characterized fluoro-bridged dimeric species. They allow the possibility of superexchange studies between metal ions, bridged by F^- ligands. Low-temperature magnetic susceptibility studies and e.s.r. spectra show the presence of weak antiferromagnetic interactions between the two high-spin Co^{II} ions, as expected for a fluoro-bridged structure.

Further interesting points of the present structure are: (i) the asymmetry in the CoF_2Co unit, caused by large differences in Co–F (axial) and Co–F (equatorial) distances; and (ii) the trigonal-bipyramidal geometry around Co^{II}, which is distorted by only 3—8° from ideal values for the angles. Ligand-field spectra show that the structure also occurs in solution in apolar solvents.

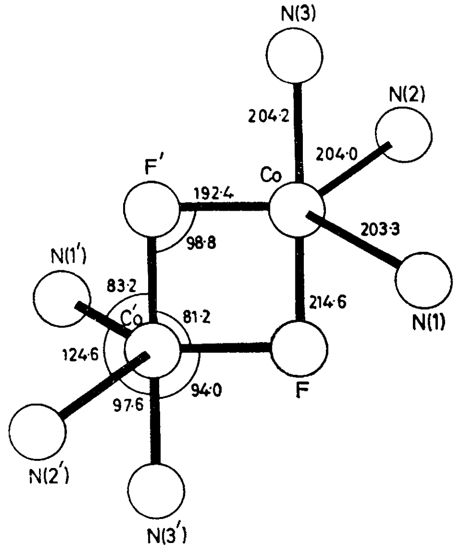


Figure. The co-ordination geometry of the dinuclear cation in μ-difluoro-hexakis-(3,5-dimethylpyrazole)dicobalt tetrafluoroborate.

In complex formation reactions of transition-metal tetrafluoroborates with sterically hindered ligands, decomposition of the BF_4^- ion often occurs, yielding F^- and BF_3 in most cases.[1] The formation of the present compounds is the first example in which the BF_4^- ions are not all decomposed.

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† Satisfactory analyses for Co, C, H, N, B, and F were obtained for all compounds.

[1] T. R. Musgrave and T. S. Lin, *J. Coordination Chem.*, 1973, **2**, 323; M. A. Guichelaar, J. A. M. van Hest, and J. Reedijk, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 999.