09.4-36 THE CRISTAL AND MOLECULAR STRUCTURE OF FLUOROMETHYLPHOSPHITO-P'-COBALAMIN.


Recently we have reported the crystal and molecular structure of dimethylphosphito-P'-cobalamin [R. Bieganowski, W. Friedrich, J. Kopf, K. von Deuten, Symposium ECM-6, Barcelona 1980]. This compound was isolated from the reaction of cyanocobalamin with trifluorophosphate in methanol. From the same reaction we isolated a second product, the title compound, which was identified and characterized by means of electrophoresis and NMR [R. Bieganowski, W. Friedrich, Z. Naturforsch. 35b, 1335 (1980)]. Now we have determined the crystal and molecular structure of this compound.

Crysalis of fluoromethylphosphito-P'-cobalamin were obtained by slow evaporation of methanol/water. The space group is P2_12_12_1 with lattice parameters: a=2570.0(14), b=2241.4(13) and c=1583.0(9) pm. The structure was refined anisotropically to R = 0.152 and wR = 0.116 for 5078 reflections.

Stereo-plot of fluoromethylphosphito-P'-cobalamin

The title compound is much less soluble in water than cyanocobalamin. In view of the good binding of fluoromethylphosphito-P'-cobalamin to the intrinsic folate-depot preparation [T. Kamikubo, R. Bieganowski, B. Senkpiel, W. Friedrich; in preparation].

09.4-37 MOLECULAR STRUCTURE OF A FOUR-COORDINATED MACROCYCIC Ni-COMPLEX [Ni(C_{26}H_{14}N_{8})]

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[Ni(C_{26}H_{14}N_{8})] crystallizes in space group P1 with cell parameters: a=3.7637(4), b=15.8254(9), c=16.5865(6) Å, α=85.67(1), γ=83.50(1), ϑ=83.16(1)°, Z=2. The Ni-atom is coordinated to four nitrogen atoms of the porphyrin-like ligand in a square planar fashion. Unlike the planar metal-prophyrin complexes, the macrocyclic ligand shows a saddle-like shape with the Ni atom at the saddle point. However, the atoms of the inner 16-membered ring are more or less in a plane. The dihedral angles pyridine/Ni-4N and benzene/Ni-4N plane are about 27° and 22°, respectively. The two Ni-N(pyridine) distances, 2.00 Å are slightly longer than the distances Ni-N(ammine), 1.86 Å. The results of the structure determination indicate that the molecular structure is as in the figure with 4 Ca double bonds. The molecular structure can be compared with a 14-membered macrocyclic iron complex, [Fe(C_{22}H_{22}N_{4})] and a 16-membered TAAB (C_{28}H_{20}N_{4}) Ni complex.

09.4-38 THE STRUCTURE OF TRIS(S-METHYLDITHIOCARBAZATE)NICHEL(III) COMPLEXES.


I. [Ni(H_{2}HNNHCSSCH_{3})]Cl_{2}, trigonal, R3, a = b = 9.875(4), c = 39.228(5) Å, D_{m} = 1.64 Mg m^{-3}, Z = 6 (Belyaeva et al., Koordaints. 14, 433). The geometry of the coordination around the Ni atom is a distorted octahedron. The Ni atom, which lies on the threefold axis, is coordinating to 2 Ni and N atoms of three bidentate S-methylthiocarbazate molecules with the formation of five-membered chelate rings. The ligand molecule is planar and has the cis-cis conformation. The Ni-N(21.409(3)Å) and Ni-N(2.141(1)Å) distances are typical for Ni octahedral S and N complexes. The sulphur and nitrogen atoms are on opposite planes with respect to the nickel atom. The interatomic distances are C-Cl(1.66(1)Å), C-N(1.34(2)Å) and S-N(1.42(1)Å) are very close to those in the free ligand (Manotti Lenfredi et al., J. Chem. Soc. Dalton Trans. (1977) 9, 417). The molecules form layers which are separated by c/3. One of the two Cl atoms is statistically distributed between two equivalent positions on the threefold axis. It was concluded that two Ni complexes contained one deprotonated S-methylthiocarbazate and the structural formula might be written down as [Ni(H_{2}HNNHCSSCH_{3})]Cl_{2}(H_{2}HNNHCSSCH_{3})].