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

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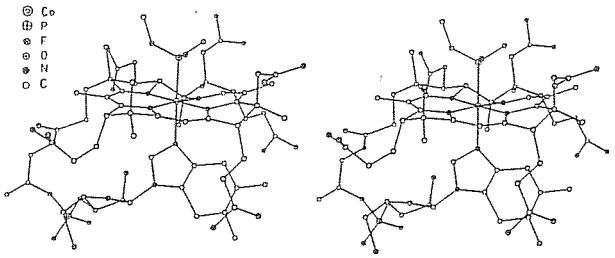
Recently we have reported the crystal and molecular structure of dimethylphosphito-P'-cobalamin [R. Bieganowski, W. Friedrich, J. Kopf, K. von Deuten, Symposium ECM-6, Barcelona 1980]. This compound was isolated from the reaction of cyanocobalamin with trifluorophosphine in methanol. From the same reaction 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.
Crystals 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 $R_w$ = 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 factor, this compound may gain some biological importance as a depot-$B_{12}$-preparation [T. Kamikubo, R. Bieganowski, B. Senkpiel, W. Friedrich; in preparation].

## 09.4-37 MOLECULAR STRUCTURE OF A FOUR-COORDINATED MACROCYCLIC Ni-COMPLEX [Ni($C_{26}H_{14}N_8$)].

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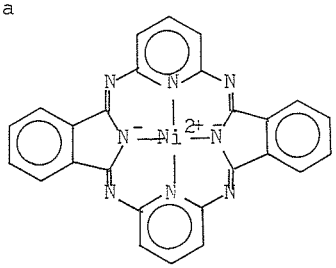
[Ni($C_{26}H_{14}N_8$)] crystallizes in space group P1 with cell parameters: a=3.7637(4), b=15.8254(9), c=16.5865(6) Å, α=85.67(1), β=83.50(1), γ=83.16(1)°, Z=2. The Ni-atom is coordinated to four nitrogen atoms of the porphyrin-like ligand in a square planar fashion. Unlike the planar metal-prophyrin 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 plane, 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(amine), 1.86 Å. The results of the structure determination indicate that the molecular structure is as in the figure with 4 C=N 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. (Hawkinson et. al., Inorg. Chem. 8, 2402 (1969)).




## 09.4-38 THE STRUCTURE OF TRIS(S-METHYLDI - THIOCARBAZATE)NICKEL(II) COMPLEXES.

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I. $[NiC_6H_{17.5}N_6S_6]Cl_{1.5}\cdot 3H_2O$, trigonal, $R\bar{3}$, a = b = 9.875(4), c = 39.228(5) Å, $D_m$ = 1.64 Mg $m^{-3}$, Z = 6 ( Belyaeva et al., Coordinatzionnaya Chimya, U.S.S.R.,(1981) 7, 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 the S and N atoms of three bidentate S-methyldithiocarbazate molecules with the formation of five-membered chelate rings. The ligand molecule is planar and has the cis-cis conformation. The Ni-S(2.409(3)Å) and Ni-N (2.14(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, C-S(1.66(1)Å), C-N(1.34(2)Å) and N-N(1.42(1)Å) are very close to those in the free ligand ( Manotti Lanfredi et al.,J.Chem. Soc.Dalton Trans.(1977) 5, 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 - methyldithiocarbazate and the structural formula might be written down as $[Ni(H_2NNHCSSCH_3)_2(H_2NNCSSCH_3)]$.