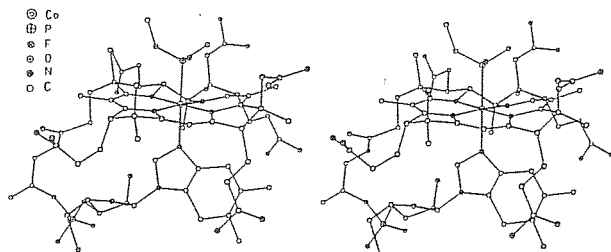


## 09.4-36 THE CRYSTAL AND MOLECULAR STRUCTURE OF FLUOROMETHYLPHOSPHITO-P'-COBALAMIN.

By R. Bieganski, Institute für Physiol. Chemie, Universität Hamburg, Grindallee 117 and J. Kopf, W. Hinrichs, K. von Deuten, Institut für Anorg. und Angew. Chemie, Universität Hamburg, Martin-Luther-King-Platz 6, D-2000 Hamburg 13, West Germany.

Recently we have reported the crystal and molecular structure of dimethylphosphito-P'-cobalamin [R. Bieganski, W. Friedrich, J. Kopf, K. von Deuten, Symposium ECM-6, Barcelona 1980]. This compound was isolated from the reaction of cyanocobalamin with tri-fluorophosphine 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. Bieganski, 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.



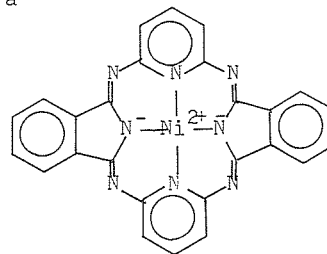
Stereo-plot of fluoromethylphosphito-P'-cobalamin

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<sub>12</sub>-preparation [T. Kamikubo, R. Bieganski, B. Senkpiel, W. Friedrich; in preparation].

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

By S. Peng, Y. Wang and T. Ho, Department of Chemistry, National Taiwan University, Taipei, Taiwan, ROC.

$[Ni(C_{26}H_{14}N_8)]$  crystallizes in space group  $P1$  with cell parameters:  $a=3.7637(4)$ ,  $b=15.8254(9)$ ,  $c=16.5865(6)$  Å,  $\alpha=85.67(1)$ ,  $\beta=83.50(1)$ ,  $\gamma=83.16(1)^\circ$ ,  $Z=2$ . 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  $27^\circ$  and  $22^\circ$  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-METHYLDITHIOCARBAZATE)NICKEL(II) COMPLEXES. By T.J. Malinowsky, V.A. Neverov, C.F. Belyaeva and V.N. Biyushkin, Institute of Applied Physics, Academy of Sciences of Moldavian S.S.R., Kishinev, U.S.S.R.

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<sup>-3</sup>,  $Z = 6$  (Belyaeva et al., Koordinatsionnaya 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-methyldithiocarbamate 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-methyldithiocarbamate and the structural formula might be written down as  $[Ni(H_2NNHCSSCH_3)_2(H_2NCCSCH_3)]$ .