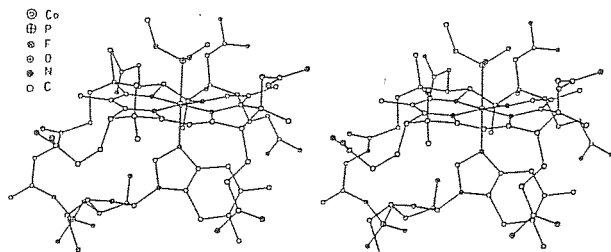


## 09.4-36 THE CRYSTAL AND MOLECULAR STRUCTURE OF FLUOROMETHYLPHOSPHITO-P'-COBALAMIN.

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.



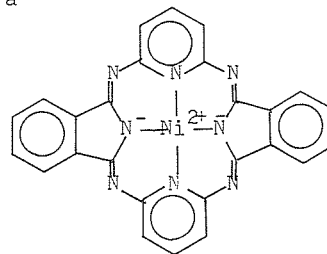
Stereo-plot of fluoromethylphosphito-P'-cobalamin

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  $[Ni(H_2NNHCSSCH_3)_2(H_2NNCSSCH_3)]$ .

. $[\text{Ni}(\text{H}_2\text{NNHCSSCH}_3)_3]_3\text{Cl} \cdot 3\text{H}_2\text{O}$ . A similar situation was found in the following compound II.  $[\text{NiC}_6\text{H}_{17.5}\text{N}_6\text{S}_6](\text{ClO}_4)_{1.5}$ , trigonal,  $P\bar{3}$ ,  $a = b = 9.670(4)$ ,  $c = 13.045(5)\text{\AA}$ ,  $Z = 2$ , with three  $[\text{ClO}_4]^-$  ions for the two Ni complexes.

One of the two  $[\text{ClO}_4]^-$  ions is statistically disordered across a center of inversion at  $001/2$ . Some bond parameters are: Ni-S = 2.386(2), Ni-N = 2.130(7), C-S = 1.672(7), C-N = 1.319(7), N-N = 1.401(9)\text{\AA}. The two crystals I and II have almost the same structure.

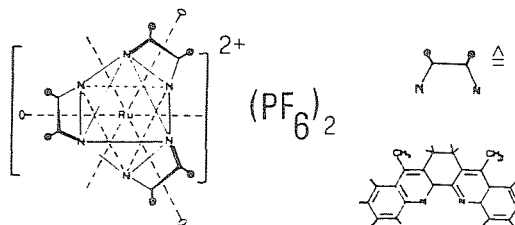
III.  $[\text{NiC}_6\text{H}_{18}\text{N}_6\text{S}_6](\text{ClO}_4)_2$ , monoclinic,  $P2_1/b$ ,  $a = 11.361(2)$ ,  $b = 22.323(5)$ ,  $c = 9.045(2)\text{\AA}$ ,  $\beta = 101^\circ 10(2)'$ ,  $Z = 4$ . Some lengths are: Ni-S = 2.370-2.393(2), Ni-N = 2.132-2.135(6), C-S = 1.650-1.667(7), C-N = 1.305-1.317(8), N-N = 1.402-1.409(8)\text{\AA}.

The  $\text{Ni}(\text{H}_2\text{NNHCSSCH}_3)_3^{2+}$  cation in this complex retains the pseudooctahedral NS coordination geometry. The difference between the complexes II and III exists in the molecular packing.

#### 09.4-40 CRYSTAL STRUCTURE OF RU-TRIS (4,7-DIMETHYL-2,3,8,9-DIBENZ-5,6-DIHYDRO-PHENANTHROLINE) DI-HEXAFLUOROPHOSPHATE.

By Margareta Zehnder, Institut für Anorg. Chemie der Universität Basel, Switzerland  
Peter Belser and Alex von Zelewsky, Institut de chimie inorganique de l'Université de Fribourg, Switzerland.

The title compound  $\text{C}_{66}\text{H}_{54}\text{F}_{12}\text{N}_6\text{P}_2\text{Ru}$  crystallizes in the trigonal space group  $P\bar{3}1c$  with  $a=b=14.180$ ,  $c=17.160$  and  $Z=2$ . The cation itself having exact  $D_3$  symmetry occupies a  $32$  special position of the space group. The structure was solved by direct methods by first eliminating the large structure factors of the metal ion. Spectroscopic data of the compound are given.



#### 09.4-39 CRYSTAL STRUCTURES OF TWO TRANS BIPYRIDINE COMPLEXES OF Ru(II), Ru(BIPYRIDINE)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub> AND Ru(4,4'-DIMETHYLBIPYRIDINE)<sub>2</sub>(PYRIDINE)<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub>;

VARIATIONS IN CONFORMATION FOR THE NECESSARILY DISTORTED TRANS BIS(BIPYRIDINE) CHELATION, By A. W. Cordes, P. N. Swepston, W. Pennington, S. M. Condren, and B. Durham, Department of Chemistry, University of Arkansas, Fayetteville, Arkansas 72701, USA.

Octahedral complexes containing two 2,2'-bipyridine (bpy) ligands generally are found to have the *cis* geometry, consistent with the expected instability of the *trans* configuration due to steric interaction between opposing  $\alpha$ -hydrogen atoms of the bpy ligands. The title cations represent the second and third structures reported of octahedral complexes with *trans* bpy groups and these, along with four square-planar di-bpy complexes, allow generalizations on the modes of accommodating the steric strain. Three of the complexes have bpy units which are in a "twist" arrangement whereby the two  $\alpha$  hydrogen atoms of each bpy move to opposite sides of the idealized  $\text{MN}_4$  plane. The other complexes display a "bowed" configuration in which the  $\alpha$  hydrogen atoms of each bpy are displaced on the same side of the plane, opposite the  $\alpha$  hydrogens of the *trans* bpy. These distortions are readily analyzed and contrasted by use of the bend and twist coordinates developed for the discussion of non-planar peptide linkages. The two title compounds are found to be in the bowed configuration, in contrast to the complex

$\text{Ru}(\text{bpy})_2(\text{H}_2\text{O})(\text{OH})^{+2}$  which has a twist conformation.

#### 09.4-41 TRIBUTYLPHOSPHINE SUBSTITUTED POLYNUCLEAR Ru-CARBONYL CARBOXYLATES. By M. Bianchi & P. Frediani, *Istituto di Chimica Organica dell'Università di Firenze*, Via G. Capponi 6, Firenze, and M. Nardelli & G. Pelizzi, *Istituto di Chimica Generale e Inorganica dell'Università di Parma*, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Via M. D'Azeglio 85, Parma (Italy).

Two new polynuclear Ru-carbonyl tributylphosphine substituted carboxylates have been synthesized by reaction of  $\text{Ru}_3(\text{CO})_{12}$  with acetic and glutaric acids respectively and subsequent treatment with tributylphosphine. Their crystal data are:

(I)  $[\text{Ru}_3(\text{CO})_4\{\text{OOC}(\text{CH}_2)_3\text{COO}\}(\text{Pbut}_3)_2]_2$ , monoclinic  $P2_1/n$ ,  $a = 16.544(10)$ ,  $b = 23.819(15)$ ,  $c = 11.046(8)\text{\AA}$ ,  $\beta = 103.72(6)^\circ$ ,  $V = 4229(5)\text{\AA}^3$ ,  $Z = 2$ ,  $D_c = 1.333\text{ g cm}^{-3}$ ,  $\mu = 8.14\text{ cm}^{-1}$  (Mo K $\alpha$ )

(II)  $[\text{Ru}_3(\text{CO})_4(\text{CH}_2\text{COO})_2(\text{Pbut}_3)]_2$ , monoclinic  $P2_1/n$ ,  $a = 14.411(8)$ ,  $b = 19.198(10)$ ,  $c = 9.665(8)\text{\AA}$ ,  $\beta = 93.45(6)^\circ$ ,  $V = 2669(3)\text{\AA}^3$ ,  $Z = 2$ ,  $D_c = 1.579\text{ g cm}^{-3}$ ,  $\mu = 12.06\text{ cm}^{-1}$  (Mo K $\alpha$ ).

Both structures were solved by single crystal diffractometer data (Mo K $\alpha$ ), and refined by full-matrix least-squares to  $R = 5.18\%$  for (I) and  $R = 3.83\%$  for (II).

The structure of (I) consists of couples of dimers  $(\text{Pbut}_3)(\text{CO})_2\text{Ru}-\text{Ru}(\text{CO})_2(\text{Pbut}_3)$  joined together by glutarate bridges coordinating to the metal atoms through their oxygens, each carboxylate group bridging two Ru atoms. Coordination around each Ru is distorted octahedral and involves two *cis* carbonyl ligands and two oxygen atoms from two carboxylate groups in a coordination plane and one phosphine and a Ru-Ru bond, 2.734(3)\text{\AA} long, *trans* with respect to that plane.