

. $[\text{Ni}(\text{H}_2\text{NNHCSSCH}_3)_3]_3\text{Cl} \cdot 3\text{H}_2\text{O}$. 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.

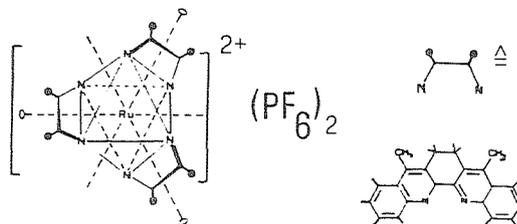
III. $[\text{NiC}_6\text{H}_{18}\text{N}_6\text{S}_6](\text{ClO}_4)_2$, monoclinic, $P2_1/b$, $a = 11.361(2)$, $b = 22.323(5)$, $c = 9.045(2)\text{\AA}$, $\beta = 101^\circ 10(2)'$, $Z = 4$. Some lengths are: Ni-S = 2.370-2.393(2), Ni-N = 2.132-2.135(6), C-S = 1.650-1.667(7), C-N = 1.305-1.317(8), N-N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

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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)₂(PPh₃)₂(PF₆)₂ AND Ru(4,4'-DIMETHYLBIPYRIDINE)₂(PYRIDINE)₂(PF₆)₂;

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 α -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 α hydrogen atoms of each bpy move to opposite sides of the idealized MN_4 plane. The other complexes display a "bowed" configuration in which the α hydrogen atoms of each bpy are displaced on the same side of the plane, opposite the α 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 Diffraattometrica del C.N.R., Via M. D'Azeglio 85, Parma (Italy)*.

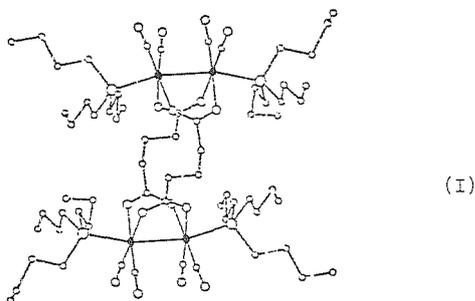
Two new polynuclear Ru-carbonyl tributylphosphine substituted carboxylates have been synthesized by reaction of $\text{Ru}_3(\text{CO})_{12}$ with acetic and glutaric acids respectively and subsequent treatment with tributylphosphine. Their crystal data are:

(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 α)

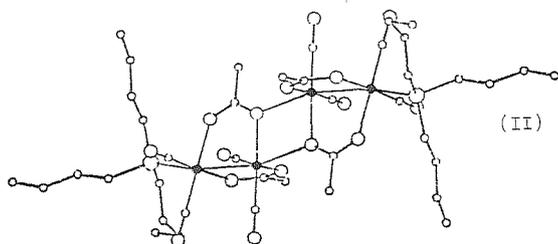
(II) $[\text{Ru}_3(\text{CO})_4(\text{CH}_2\text{COO})_2(\text{Pbut}_3)]_2$, monoclinic $P2_1/n$, $a = 14.411(8)$, $b = 19.198(10)$, $c = 9.665(8)\text{\AA}$, $\beta = 93.45(6)^\circ$, $V = 2669(3)\text{\AA}^3$, $Z = 2$, $D_c = 1.579\text{ g cm}^{-3}$, $\mu = 12.06\text{ cm}^{-1}$ (Mo K α).

Both structures were solved by single crystal diffractometer data (Mo K α), 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.



Tetranuclear complexes are found also in (II), but their structure is now different: two couples of dimers $(\text{Pbut}_3)(\text{CO})_2\text{Ru}-(\text{CH}_3\text{COO})_2-\text{Ru}(\text{CO})_2$ are centrosymmetrically joined together by oxygen bridges formed by acetate groups. So there are two kinds of Ru atoms having different ligand environment, and two kinds of acetate groups differing because in one of them one oxygen atom coordinates to two metal atoms. As found in (I) both acetate groups chelate a couple of bonded metal atoms, $\text{Ru}-\text{Ru} = 2.682(2)$ Å. Coordination around one Ru is quite similar to that found in (I), while around the other Ru the bridging carboxylate oxygen replaces the phosphorus ligand.



09.4-42 THE CONFORMATION AND RING STRAINS OF CHELATES IN $\text{M}(1,3\text{-PDTA})$ TYPE COMPLEXES. By R. Herak and G. Srdanov, Laboratory of Solid State Physics and Radiation Chemistry, "Boris Kidrič" Institute, Belgrade, and M. Djuran and D. Radanović, Faculty of Sciences, University "Svetozar Marković", Kragujevac, Yugoslavia.

In order to determine the influence of the size of metal ion on strain in chelate rings of $\text{M}(1,3\text{-PDTA})$ complexes ($\text{M} = \text{Co}, \text{Cr}, \text{Rh}$, 1,3-PDTA = 1,3-propanediaminetetraacetate) and to verify the components of the CD spectrum of the Rh complex, the crystal structures of $\text{Na}[\text{Cr}(1,3\text{-PDTA})] \cdot 3\text{H}_2\text{O}$ (I) and $(-)\text{-D-Na}[\text{Rh}(1,3\text{-PDTA})] \cdot 3\text{H}_2\text{O}$ (II) were investigated.

The crystals of I and II are isomorphous and belong to the orthorhombic system, with cell dimensions $a=16.514(5)$, $b=8.809(2)$, $c=11.429(3)$ Å and $a=16.553(5)$, $b=8.853(2)$, $c=11.451(3)$ Å, respectively, $Z=4$, space group $\text{P}2_12_12_1$. The crystal structure analyses have been based on 1699 (I) and 2928 (II) diffractometer data. The heavy atom method and the full-matrix least-squares technique were applied. Final R is 0.057 (I) and 0.030 (II).

The crystal structure consists of the complex and of the sodium ions and molecules of water. The metal ion is coordinated octahedrally by a hexadentate 1,3-PDTA ligand, and the complex possesses one six- and four five-membered rings. In both structures, the six-membered 1,3-propanediamine chelate ring takes a twist-boat δ conformation, two equatorially disposed glycinate G rings have an envelope λ conformation and two glycinate R rings in axial position have slightly puckered or envelope δ conformations.

The absolute configuration of II can be designated as $\Lambda\Lambda\Lambda$. The absolute configuration of I, a crystal selected by chance from optically inactive complex, is also $\Lambda\Lambda\Lambda$.

The ring strains have been determined and compared with those in related cobalt(III) complexes (Nagao, Marumo and Saito, Acta Cryst. (1972) B28, 1852; Kalina, Pavelčík and Majer, Collect. Czech. Chem. Commun. (1978) 43, 3140). There is a significant difference in strain between the two G rings in complexes I and II, which otherwise have a quasi-twofold axis. The data indicate that the ring strains are not simply related to the size of the metal ion but that crystal packing effects may also have some influence.

09.4-43 NEW HYDRIDO-BRIDGE BINUCLEAR RHODIUM-IRIDIUM COMPLEXES. By A. Albinati, H. Lehner, R. Nægeli, A. Musco and L. M. Venanzi. *Institute of Chemistry, Polytechnic, Milano, Italy and Laboratory for Inorganic Chemistry, E.T.H., Zürich, Switzerland.

Many examples of hydrido-bridged bi-homometallic complexes are already known, but only few examples of heterometallic compounds have been so far reported. Here we will discuss the X-ray structures of two hydrido bridged binuclear Rh-Ir complexes: [diphospho Rh(μH)₃Ir(PET_3)₃]⁺ (BPh_4)⁻ (I) and (PET_3)₂Rh(μH)(μCl)Ir(PET_3)₂H₂ (II); they are representative members of a new series of hydrido heterometallic compounds. The geometry of the cation (I) is shown in the figure. Compound (II) has a mixed hydrido-chloride bridged structure; the coordination around the Ir is a distorted octahedron with two P atoms trans to each other, that around Rh is square planar. The details of the structure and the spectroscopic evidences (NMR) for the presence and location of the hydrogens will be discussed.

Crystallographic Data: (I), $a=12.728(3)$, $b=17.340(3)$, $c=31.532(4)$ Å, $\beta=109.3(1)^\circ$, $\text{P}2_1/c$, $Z=4$; relevant distances: Ir-Rh 2.636(2), Ir-P1 2.352(4), Ir-P2 2.299(6), Ir-P3 2.334(4), Rh-P4 2.157(5), Rh-P5 2.194(5) Å. (II) $a=11.507(4)$, $b=15.974(5)$, $c=19.198(5)$ Å, $\beta=103.2(1)^\circ$, $\text{P}2_1/c$, $Z=4$; relevant distances: Ir-Rh 2.899(1), Ir-Cl 2.494(3), Rh-Cl 2.427(3), Ir-P1 2.263(4), Ir-P2 2.272(4), Rh-P3 2.199(3), Rh-P4 2.245(3) Å.