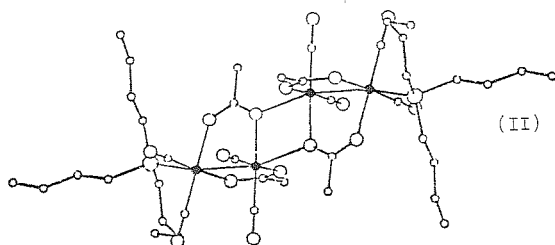


Tetranuclear complexes are found also in (II), but their structure is now different: two couples of dimers $(\text{Pbut}_3)(\text{CO})_2\text{Ru}-(\text{CH}_3\text{COO})_2-\text{Ru}(\text{CO})_2$ are centrosymmetrically joined together by oxygen bridges formed by acetate groups. So there are two kinds 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.

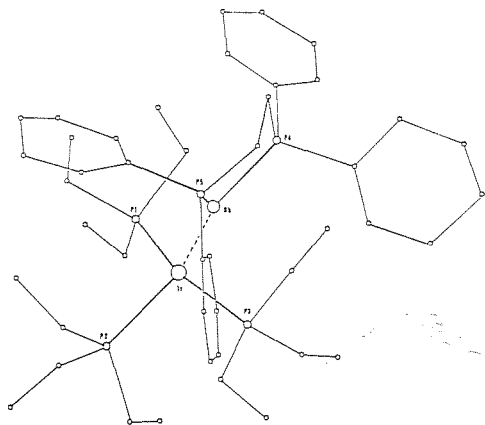
The absolute configuration of II can be designated as $\Lambda\Lambda\Lambda$. The absolute configuration of I, a crystal selected by chance from optically inactive complex, is also $\Lambda\Lambda\Lambda$.

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. Nägeli, 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.



Molecular structure of cation (I)
(diphosph = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$).

The $[\text{Rh}_2(\text{TMB})_4\text{Cl}_2](\text{PF}_6)_2$ crystals are orthorhombic,

space group Pbcn (No. 60), $a=13.846$, $b=24.773$, $c=17.068$ Å, $Z=4$. The structure was solved by a combination of Patterson and direct methods. Convergence was obtained in a full-matrix least-squares refinement (anisotropic Rh, Cl, C, N, P, F, constrained isotropic H, $R=0.12$, $R_w=0.078$, 1903 reflections with $F > 1.5\sigma(F)$) with a partially disordered ligand molecule. The bonded Rh atoms are related by a twofold axis, and the Rh-Rh vector is closely aligned with the c axis. Thus the orientation of the molecule is suitable for a single-crystal spectroscopic study of the formal Rh-Rh single bond (Rh-Rh, 2.77 Å, compared to 3.26 Å in the corresponding Rh (I) complex.)

$[\text{Ir}_2(\text{TMB})_4\text{I}_2](\text{BPh}_4)_2$ crystallizes in the orthorhombic

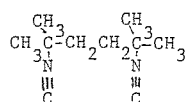
space group Pccn (No. 56), $a=15.141$, $b=28.104$, $c=23.877$ Å, $Z=4$. Although 9019 unique reflections were measured many of the intensities were low, and the quality of fit is not as good as in the Rh structure. The Ir and I atoms occupy special positions ($1/4$ $1/4$ z). Serious questions remain concerning possible disorder within the molecule, but the bonding arrangement, and the Ir-Ir distance of 2.82 Å, are confirmed.

We are indebted to the U.S. and Swiss National Science Foundations for support of this work, and to Jack D. Dunitz, K.N. Trueblood, Paul Seiler, Richard E. Marsh, Harry B. Gray, and Carolyn Knobler for assistance and advice.

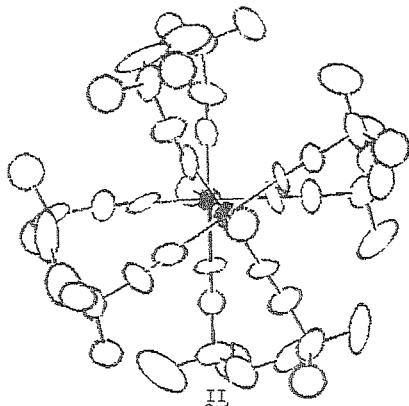
09.4-44 CRYSTAL STRUCTURE ANALYSES OF BINUCLEAR RHODIUM (II) AND IRIIDIUM (II) ISOCYANIDE COMPLEXES. By A.W. Maverick and T.P. Smith, California Institute of Technology, and E. Maverick, University of California, Los Angeles.

We have determined the crystal structures of $[\text{Rh}_2(\text{TMB})_4\text{Cl}_2](\text{PF}_6)_2$ and $[\text{Ir}_2(\text{TMB})_4\text{I}_2](\text{BPh}_4)_2$ (TMB=

2,5-diisocyano-2,5-dimethylhexane, I), both of which involve a propeller-like arrangement of the bridging diisocyanoalkane ligands about the central X-M-M-X unit. The two approximately planar $\text{M}(\text{CNR})_4$ moieties are partially staggered, with average C-M-M-C torsion angles of 32° (M=Rh) and 30° (M=Ir). These angles are identical (within experimental error) to those found in the corresponding Rh (I) complex (Mann, K.R., Thich, J.A., Bell, R.A., Coyle, C.L., and Gray, H.B., *Inorg. Chem.* (1980) **19**, 2462-2468). An Ortep drawing of the cation (II) appears below.



I



II

09.4-45 MIXED VALENCE COMPLEXES OF PLATINUM. THE CRYSTAL STRUCTURES OF $[\text{Pt}(\text{Meen})_2][\text{PtBr}_2(\text{Meen})_2](\text{ClO}_4)_4$ AND $[\text{Pt}(\text{tn})_2][\text{PtI}_2(\text{tn})_2](\text{ClO}_4)_4$. Bernd Keppler and Barbara Müller, Anorganisch-Chemisches Institut der Universität, 69 Heidelberg 1, BRD. Mario Cannas and Gaime Marongiu, Istituto Chimico dell'Università, 09100 Cagliari, Italy.

We have performed single crystal diffraction studies of the title compounds mainly to determine the geometry of the linear chains showing alternating Pt(II) and Pt(IV) atoms. Both compounds occur as coloured, lustrous metallic, fine needles. $[\text{Pt}(\text{Meen})_2][\text{PtBr}_2(\text{Meen})_2](\text{ClO}_4)_4$ (Meen = 1,2-diaminopropane) is orthorhombic (Pc2a) with $a = 7.74(1)$, $b = 11.14(2)$, $c = 17.42(3)$ Å and $Z = 2$; a total of 1800 data were collected to $2\theta = 52^\circ$. $[\text{Pt}(\text{tn})_2][\text{PtI}_2(\text{tn})_2](\text{ClO}_4)_4$ (tn = 1,3-diaminopropane) is monoclinic (P2) with $a = 10.29(2)$, $b = 11.33(2)$, $c = 8.62(1)$ Å, $\beta = 125.7^\circ$, $Z = 1$. A total of 1700 data were collected. Most crystals are twinned along [010] simulating a pseudo-orthorhombic symmetry with a centered cell very close to that reported for Br and Cl derivatives. Pt(Meen)₂ and Pt(tn)₂ groups in the crystals of the two compounds stack with the molecular plane perpendicular to the b axis, which results in a linear Pt(II) \cdots X-Pt(IV)-X \cdots chain. At this stage of refinement ($R \approx .10$) the Pt(II)-Pt(IV) spacings in each structure are equal ($\frac{1}{2}b$) although not required crystallographically. The difference in metal-metal separation between the two compounds is due to corresponding differences in the direct M-X bonds (Pt-Br=2.52 Å; Pt-I = 2.66 Å); the lengths of the charge-transfer Pt \cdots X are rather unaffected.