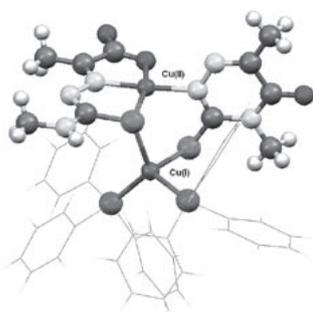


P07.01.13*Acta Cryst.* (2008). A64, C403**Bis(tpp)copper(I) thiosemicarbazones: Unexpected chemistry revealed by X-ray diffraction**

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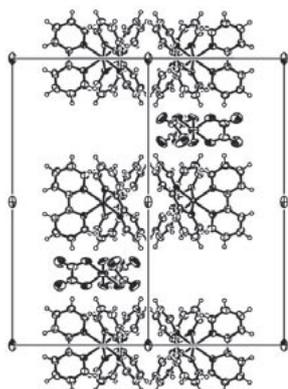
Starting from bis(triphenylphosphine)copper(I) salts and from methylpyruvate thiosemicarbazone we have planned the synthesis of several complexes. The choice has fallen on these compounds for two main reasons: first, triphenylphosphines are known to stabilize copper in its lower oxidation state and, second, tertiary phosphines seem to enhance the solubility of Cu(I) thioamide complexes. The overwhelming majority of analogous compounds present the ligand that behaves as monodentate through the sulphur atom, in agreement with the soft nature of copper(I), and the remaining fourth position occupied by a halide. We have recently demonstrated that it is the presence or absence of soft ligand competitors that influence the coordination mode of thiosemicarbazones and not the protonation of the azinic nitrogen that renders them monodentate. In the course of these studies we have met with spectral and analytical anomalies that have been clarified by X-ray crystallography. A few compounds contain copper clusters, others contain ligands that have partially undergone a cyclization and in two cases linear and cyclic ligands bind two copper centres in two different oxidation states.



Keywords: copper coordination compounds, mixed-valence transition-metal compounds, clusters in coordination complexes

P07.01.14*Acta Cryst.* (2008). A64, C403**Porous structure of bis{tris(bipyridine)ruthenium(II)} tris(oxalato)cobaltate(III) chloride**Hiroshi Miyamae¹, Ayumi Sato¹, Satoshi Tachiyashiki², Goro Hihara¹
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Slow mixing of water solutions of [Ru(bpy)₃]Cl₂ (bpy=bipyridine) with K₃[Co(ox)₃] (H₂ox=oxalic acid) gave red block title crystals. It crystallizes in hexagonal, space group *P*6₃22, with *a*=13.0506(3) Å and *c*=24.1223(5) Å. The unit cell contains two metal complex sandwiches in which [Co(ox)₃]³⁻ anion is sandwiched by two [Ru(bpy)₃]²⁺ cations and two Cl⁻ ions they are surrounded by six bpy moieties of different Ru complexes (Figure below: showing the unit cell



projection along the (110) direction). The stack forms big void which can store the volume of [Co(ox)₃]³⁻ anion.

Keywords: ruthenium compound, cobalt compound, porous structure

P07.01.15*Acta Cryst.* (2008). A64, C403**Structural study of hydride and dihydrogen ligands ruthenium complexes: Reversible hydrogen release**

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The widespread use of dihydrogen as an energy carrier for onboard applications is an important challenge for economical and environmental issues. Selective activation and functionalization of alkanes is also a continuing area of interest, and efficient production of dihydrogen through catalyzed dehydrogenation of abundant hydrocarbons would be very valuable. An attractive goal is to combine inorganic hydrides and organic compounds as a source of hydrogen materials. We first isolated a new bis(dihydrogen) complex RuH₂(η²-H₂)₂(PCyp₃)₂, (1) characterized by NMR, single-crystal X-ray and neutron diffraction. The neutron diffraction study is the first carried out for a bis(dihydrogen) complex.[1] We present as well the X-ray structures of two new Ru complexes: the Ru(0) complex [Ru{PCyp₂(h₂-C₅H₇)₂(h₂-C₂H₄)], and the trans dihydride [RuH₂{PCyp₂(η²-C₅H₇)₂]. Both structures show the dehydrogenation of one cyclopentyl ring of each phosphine ligand. [2] The formulation of each complex has been ascertained by an X-ray structural study. Each experiment was carried out at 100 K, in order to prevent dihydrogen rotation, and to help the localisation of the hydrogen atoms around the ruthenium. We have observed an easy partial dehydrogenation of the phosphine ligands in 1, leading in a first step to equilibrium between dihydride complexes. A subsequent dehydrogenation process leads to a new Ru(0) complex. Ten hydrogen atoms have been removed from 1, which represents 1.71% of the weight of the complex. We have demonstrated that the process is fully reversible under very mild conditions. Complex 1 can serve as a model for hydrogen storage.

[1] M. Grellier et al, JACS, 2005,127, 17592 -17593.

[2] M. Grellier et al, Angew. Chem. Int. Ed., 2007, 46, 2613-2615.

Keywords: hydride compounds, dihydrogen complexes, X-ray structure determination

P07.01.16*Acta Cryst.* (2008). A64, C403-404**Synthesis, structure, and reactivity of ruthenium-zinc trinuclear hydrides with phosphine ligands**Tsuneaki Yamagata¹, Yukitsugu Maeda¹, Hideaki Miyake¹, Yasutaka Kataoka², Kazuhide Tani³¹Osaka University, Department of Chemistry, Graduate School of Engineering Science, Machikaneyama 1-3, Toyonaka, Osaka, 560-8531, Japan, ²Nara Women's University, Nara, 630-8506, Japan, ³Higashiosaka College, Nishitutum Gakuen-chou 3-1-1, Higashiosaka, Osaka 577-8567, Japan, E-mail: qq5b5szd@coast.ocn.ne.jp

New heteropolymetallic hydride-bridged complexes, [(L)₃Ru(μ-H)₃]₂Zn {L = 1/3 triphos (triphos = CH₃C(CH₂PPh₂)₃) and PPh₃},