Experimental report

26/09/2015

Proposal:	**5-12-304**	**Council:**	4/2014
Title:	Charge density in a polypyridine molecule		
Research area:	Chemistry		

This proposal is a new proposal

Main proposer:	**Eberhardt HERDTWECK**
Experimental team:	Cornell HERDTWECK Alexander POETHIG Eberhardt HERDTWECK
Local contacts:	Marie Helene LEMEE CAILLEAU Sax Anton MASON

Samples: $C_{26}H_{19}N_5$

Instrument	Requested days	Allocated days	From	To
D19	5	5	28/08/2014	03/09/2014
D9	0	0		

Abstract:

Polypyridine complexes of Ru and Os are promising polymetal complexes for light-harvesting components (photoelectrochemical solar cells) or models for photosynthetic centres. (E. Figgemeier et al. in Dalton Trans. 2004,,1918-1927) Our group interests are focused on non-classical hydrogen bonds, agostic interactions, weak Cl-H, C-H, N-H and O-H bonds and charge density calculations. To understand the solid state behaviour in detail of the title compound it is necessary to determine very accurately the hydrogen, carbon and nitrogen positions and ADP's in the five pyridine moieties. X-N calculations will help us in determining the charge densities. X-ray high resolution data have been measured up to d-spacings of 0.50 Å. Further information is given in the appended PDF-files.

EXPERIMENTAL REPORT

EXPERIMENT N° 5-12-304
INSTRUMENT D19

DATES OF EXPERIMENT:
28th August – 3rd April 20147

TITLE: Charge density in a polypyridine molecule

EXPERIMENTAL TEAM
Eberhardt Herdtweck, Connie Herdtweck
Anorganisch-Chemisches Institut, Lichtenbergstrasse 4,
D-85747 Garching,Germany.

Local contacts:
Sax Mason, Marie-Hélène Lemée-Cailleau, and Estelle Mossou
Institut Laue Langevin, 71 Avenue des Martyrs, 38042 Grenoble Cedex 9, France.

Background

Polypyridine complexes are compounds in which a polypyridine, such as 2,2'-bipyridine, 1,10-phenanthroline, or 2,2';6'2"-terpyridine, coordinates to a metal ion.

Polypyridine compounds are multidentate ligands which have characteristic properties, such as photosensitization. The complexes are very stable to light, electricity, and heat because the bonds between the central metal ion and polypyridine ligands are usually very strong; furthermore, the polypyridine itself is generally very stable. The compounds have peculiar optical, electrochemical, and magnetic properties. Some complexes exhibit a strong absorption band in the visible light region, which is called metal-to-ligand charge transfer (MLCT) or ligand-to-metal charge transfer (LMCT). The properties of the complexes can be tuned easily by introducing substituents, for example, electron donation, electron withdrawal, and π-conjugating groups, to the polypyridine moiety. The MLCT absorption band can be shifted, the emission wavelength can be changed, and the emission lifetime can be extended (see e.g. Wikipedia)

A well-known example of a polypyridine complex is rutheniumtris(bipyridine), $Ru[(bpy)_3]^{2+}$. This complex exhibits intense luminescence at room temperature in aqueous solution. Another example is a platinum-bipyridine-dithiolate complex, Pt(bpy)(bdt), in which bdt denotes a 1,2-benzenedithiolate anion. This complex also exhibits photoluminescence at room temperature, and its wavelength and lifetime can be tuned by substitution of either bipyridine or dithiolate moieties. Structural control is easier than for ruthenium complexes due to the square planar structure of the platinum complex.

Aims of the experiment:

To understand the solid state behaviour of the title compound in detail it is necessary to determine very accurately the hydrogen, carbon and nitrogen positions and ADP's in the five pyridine moieties. X-N calculations will help us in determining the charge densities. X-ray high resolution data have been measured to a d-spacing of 0.50 Å. If we know the charge density of the ligand we can better understand the chemical and physical behaviour of the polymetal complex. We can predict which metal will be the best to give a very stable complex.

Our group interests are focused on non-classical hydrogen bonds:

Nonclassical vs Classical Metal···H_3C–C Interactions: Accurate Characterization of a 14-Electron Ruthenium(II) System by Neutron Diffraction, Database Analysis Solution Dynamics and DFT Studies
Walter Baratta, Carlo Mealli, Eberhardt Herdtweck, Andrea Ienco, Sax A. Mason, and Pierluigi Rigo
J. Am. Chem. Soc. **2004**, *126*, 5549-5562.
ILL report **2004**, , 44-45. (Scientific Highlight)

Agostic interactions:

$[RuCl_2\{PPh_2(2,6\text{-}Me_2C_6H_3)\}_2]$: A Neutral 14-Electron Ruthenium(II) Complex with Two Agostic Interactions
Walter Baratta, Pierluigi Rigo, and Eberhardt Herdtweck
Angew. Chem. Int. Ed. Engl. **1999**, *38,* 1629-1631.

Weak Cl-H, C-H, N-H and O-H interactions:

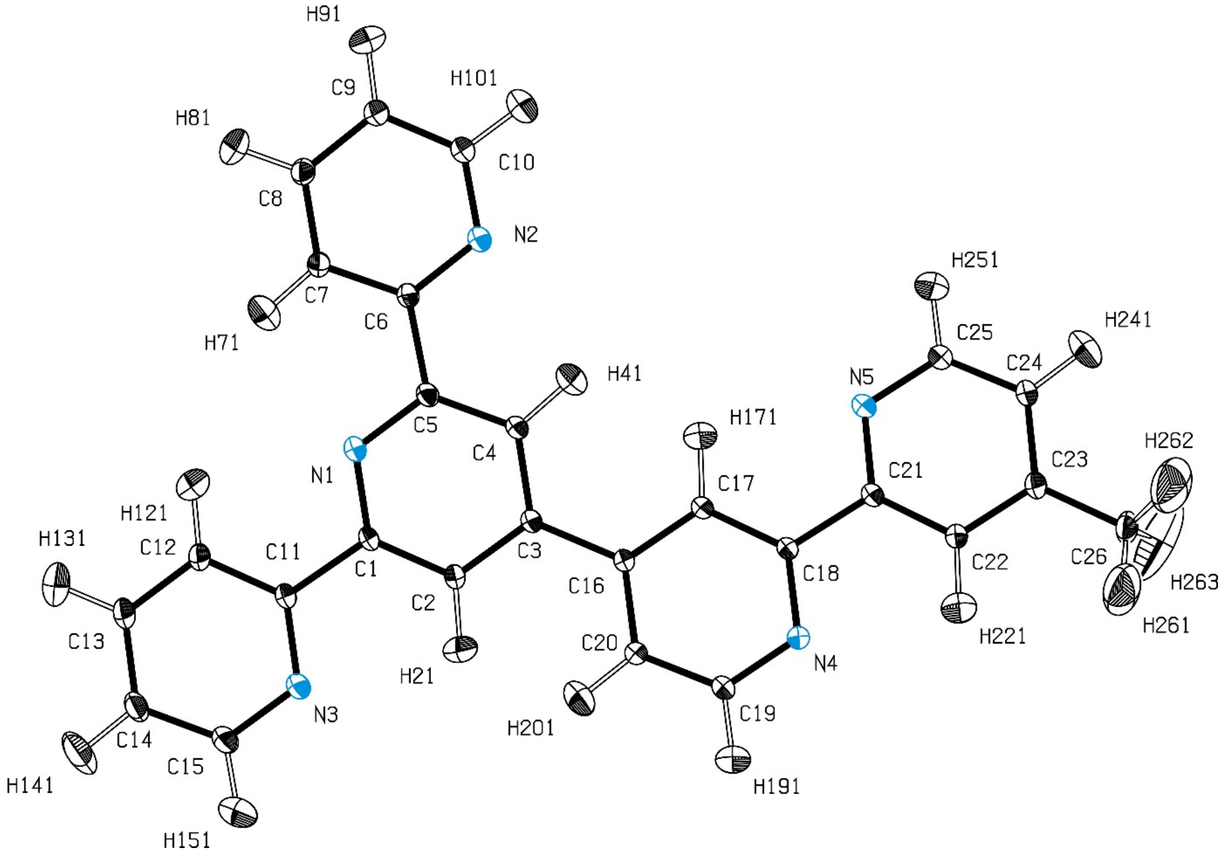
Square-Planar Iridium(II) and Iridium(III)-Amido Complexes Stabilized by a PNP Pincer Ligand
J. Meiners, M. G. Scheibel, Marie-Hélène Lemée-Cailleau, Sax A. Mason, M. Bele Boeddinghaus, Thomas F. Fässler, Eberhardt Herdtweck, **Marat M. Khusniyarov**, and **Sven Schneider**
Angew. Chem. Int. Ed. **2011**, *50,* 8184-8187.
ILL report **2011**, , 28-29. (Scientific Highlight)
CNN Pincer Ruthenium Catalysts for Hydrogenation and Transfer Hydrogenation of Ketones: Experimental and Computational Studies
Walter Baratta, Salvatore Baldino, Maria José Calhorda, Paulo J. Costa, Gennaro Esposito, Eberhardt Herdtweck, Santo Magnolia, Carlo Mealli, Abdelatif Messaoudi, Sax A. Mason, and Luis F. Veiros
Chem. Eur. J. **2014**, *20*, 13603-13617.

Final work:

The experiment was straight forward but with a reduced power of the reactor. In consequence the final R-values are not brilliant (R1=0.0718 (4839 2sigI data), 0.0940 (all 6360 data), and wR2=0.217. 1/3rd of the reflections were flagged as less thans or negative. Nevertheless, the results are satisfying and all hydrogen atoms could be located in a proper way. Therefore, the C/N assignments were proofed.

The final results will be published ASAP.

Dr. Eberhardt Herdtweck


H91
H101
C9
H81
C10
C8
N2
H251
C7
C6
H71
C25
H241
C24
N5
H41
H171
C5
C4
H262
N1
C23
C21
C17
H121
H131
C12
C11
C1
C3
C2
C16
C18
C22
C26
H263
H261
C13
H221
C20
H21
N4
N3
C14
C15
C19
H201
H141
H191
H151