

Mixed-metal Ag(I)/Co(III) complexes

Ryan M. Hellyer^a, Sally Brooker^a, Leonard F Lindoy^b, David S. Larsen^a

^a University of Otago, Dunedin, New Zealand
^b University of Sydney, NSW, Australia



An important objective in crystal engineering is the construction of multi-component systems. Here we present **silver(I)** and **cobalt(III)** complexes and a mixed-metal **Silver(I)/Cobalt(III)** complex built by using the **cobalt(III)** complex as a sub-unit.

Ligand Synthesis

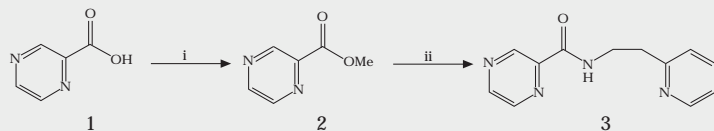


Figure 1: Ligand synthesis. Reagents and conditions:

- (i) MeOH, SOCl₂
(ii) 2-(2-aminoethyl)pyridine/N

The ligand pyrazine-2-carboxylic acid (pyridine-2-ylethyl)-amide (L) was prepared by converting 2-pyrazine carboxylic acid (1) to its methyl ester analogue (2) through the use of methanol and thionylchloride. 2-(aminoethyl)pyridine (3) was added with stirring. Evaporation to dryness followed by Si gel column chromatography resulted in a white solid in quantitative yield.

¹H NMR (300 MHz, CDCl₃): •(ppm) = 9.33 (s, 1H), 8.79 (s, 1H), 8.74 (s, 1H), 4.06 (s, 3H).

Cobalt(III) Complex

Reaction of (4) with cobalt(II)tetrafluoroborate in 2 : 1 molar ratio with triethylamine added as base resulted in the formation of an orange/red coloured solution. Slow diffusion of diethyl ether into this solution formed microanalytically pure, deep red, plate shaped analytically pure crystals in 84.3% yield.

The structure showed that the Co(II) metal ion had oxidized to Co(III) on complexation and bound in a distorted octahedral geometry. The ligand L_{3py} is bound in a *mer* arrangement by all 3 N atoms of each ligand.

Each unit cell contains an acetonitrile with a nitrogen atom disordered over two sites with 50% occupancy, another acetonitrile molecule and one tetrafluoroborate anion rotationally disordered over two sites with 76 and 24% occupancy. There were no hydrogen bonds present in the crystal structure

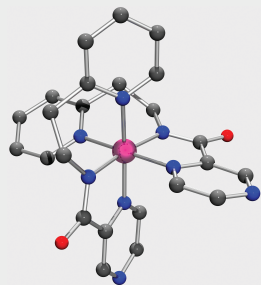


Figure 2: Ligand synthesis. Reagents and conditions:

Silver(I) Complexes (B) and (C)

Reaction of (4) with silver(I) tetrafluoroborate or silver(I) nitrate in 1 : 1 molar ratio resulted in a lemon coloured solution. Diffusion of diethyl ether into the solutions gave microanalytically pure clear colourless rod shaped crystals in yields of 68% (B) and ???% (C). The X-Ray crystal structure of the tetrafluoroborate compound was obtained.

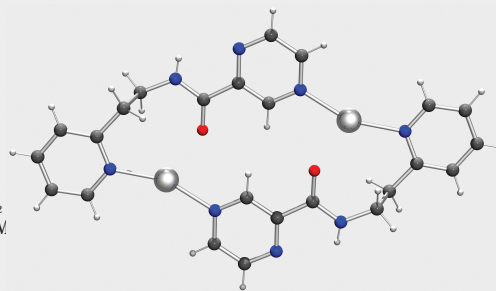


Figure 3: Ligand synthesis. Reagents and conditions:

The resulting complex consisted of two Ag(I) ions and two ligands. The Ag(I) The Ag(I) atoms were bound two the pyridine N atom of each ligand in a distorted linear geometry with a long (???) A bond to the O atom of one ligand. The structure consisted of a single

Mixed-metal Co(III)/Ag(I) Complex

Complexation of (A) with Ag(I) in a 1 : 1 ratio in acetonitrile followed by diethyl ether diffusion into the brown/red coloured solution gave brown/red block like crystals in 21% yield. Elemental analysis indicated that the product obtained was infact the 4 : 1 cobalt(III) complex to silver(I).

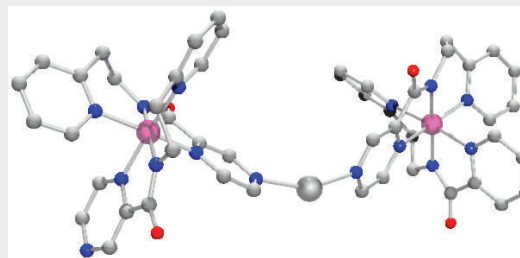


Figure 4: Ligand synthesis. Reagents and conditions:

The cobalt(III) complex was also re-complexed with silver(I) nitrate in 1 : 1 ratio, the intention being to block potential binding points to the Ag(I) to limit the number of possible conformations allowed. On complexation in acetonitrile no change was observed. Diethyl ether was diffused into the solution which afforded spiky red/brown crystals and some very small white crystals. The white crystals were assumed to be silver tetrafluoroborate or similar inorganic salt, it was assumed to not be silver nitrate as this is soluble in both acetonitrile and diethyl ether.

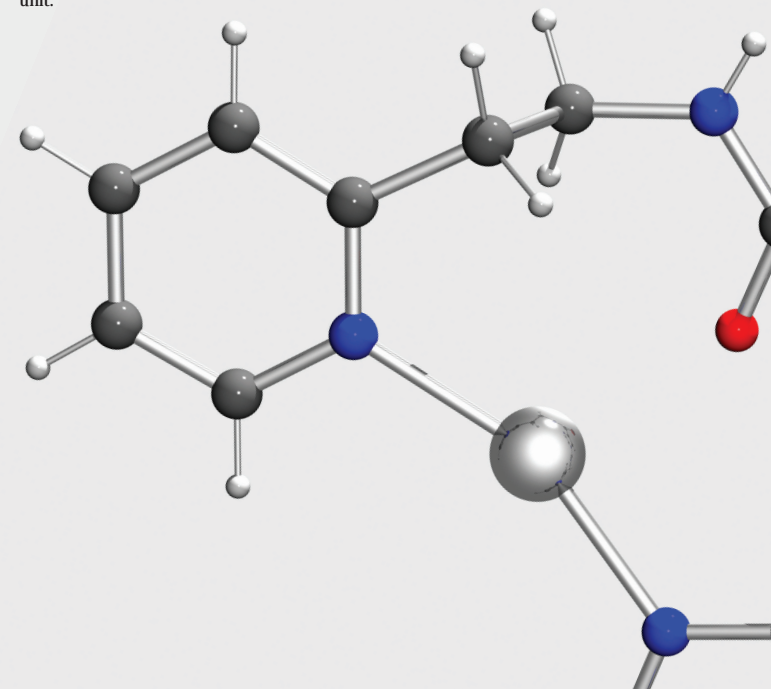
Cobalt(III) Complex

The cobalt(III) complex was prepared by 2 : 1 : 1 reaction of cobalt(II) tetrafluoroborate, L and triethylamine as base in acetonitrile. Crystals suitable for X-ray crystallography were prepared by slow diffusion of diethyl into the crude acetonitrile solution.

X-ray crystallography showed that the cobalt(II) oxidised to cobalt(III) on complexation. The cobalt(III) was bound in an octahedral geometry in a *mer* arrangement by all 3 N atoms of each ligand. The mean planes of the pyridine and pyrazine rings of each ligand were in a twisted conformation with a dihedral angle between the planes of 42.03 and 40.45°. The O atom of each ligand is pointing away from the metal center.

Future

The magnetic properties of these compounds will be analysed. Comparisons will be made between the mono-metallic complexes and the mixed-metal complex to determine whether the properties of the individual components effect the magnetic properties of the larger unit.



Otago

Acknowledgements

I Stewart, Jonathan A. Kitchen, Dr Andy and ?. Noble for help with X-Ray crystal structure determination. Dr Jason R. Price for help with the preparation of POV-Ray images.

References

Still need to get three or four references to place here. These will be coming soon!