Experimental report

26/08/2016

Proposal: 5-51-506 **Council:** 10/2014

Title: Spin density in a Ni(III) complex with spin S=1/2

Research area: Chemistry

This proposal is a new proposal

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Samples: (CH3P(Ph)3)[(NibdtCl2)2]

Instrument	Requested days	Allocated days	From	To
D3 High field >1T	12	10	25/06/2015	05/07/2015
D19	3	3	18/06/2015	22/06/2015

Abstract:

A new method was recently developed for the combined refinement of a unique electron density model, based on the data provided by three complementary techniques: high resolution X-ray diffraction (HRXRD), polarised neutron diffraction (PND) and neutron diffraction (ND). It allows modelling both charge and spin densities from these three data sets and provides spin-resolved electron densities.
We have performed a charge density study of a complex of the Ni(III) ion with two bidentate ligands having a radical character at 100K by HRXRD and a structural determination at 15K by ND on D19 (5-12-278) providing precise hydrogen distances for the charge density analysis. We ask for 12 days on the D3 polarised neutron diffractometer in order to measure the flipping ratios at 2K under 9T in the paramagnetic phase (S=1/2) and 3 days on D19 in order to determine the precise nuclear structure at 2K for the sample that will be used on D3 (different from the one previously used on D19).
The proposal is focused on a comparison between the theoretical and experimental joint refinement of charge and spin densities.
Extensive theoretical DFT calculations on this compound have already been performed.

Experimental

This study is part of the ongoing project with an aim of mutual comparison of the theoretical and experimental spin densities.

Studied complex of $(CH_3P(Ph)_3)[Ni(bdtCl_2)_2]$ (methyl triphenylphosphonium bis (3,6-dichlorobenzene-1,2-dithiolato) nickelate(1-) is square planar with Nickel in oxidation state III. Ligands can have radical character (so-called non-innocent ligands). Crystal structure consists of two anions $(NibdtCl_2)^-$ in special position and counter cation $(CH_3P(Ph)_3)^+$.

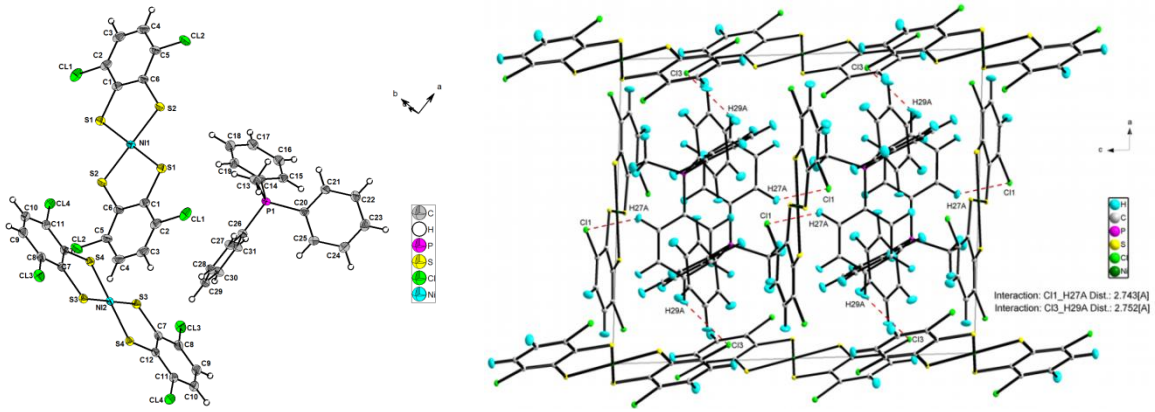


Fig.1: (a) Ortep drawing for $(CH_3P(Ph)_3)[Ni(bdtCl_2)_2]$, Thermal ellipsoids are drawn at 30% probability.

(b) Crystal packing: Projection of the crystal structure **,** along *b* axis.

Three different techniques were used: neutron diffraction (ND), X-Ray Diffraction (XRD) and polarised neutron diffraction (PND). XRD data collection was performed on an Oxford Diffraction Gemini R four circle diffractometer, using Mo-Kα radiation at 100(1) K, data collections for ND and PND were performed at 2 K on D19 and D3 respectively at Institut Laue–Langevin, Grenoble. Multipole refinement and the topological analysis were performed using XD2006 program package. Spin density analysis was performed with FullProf.

Preliminary results:

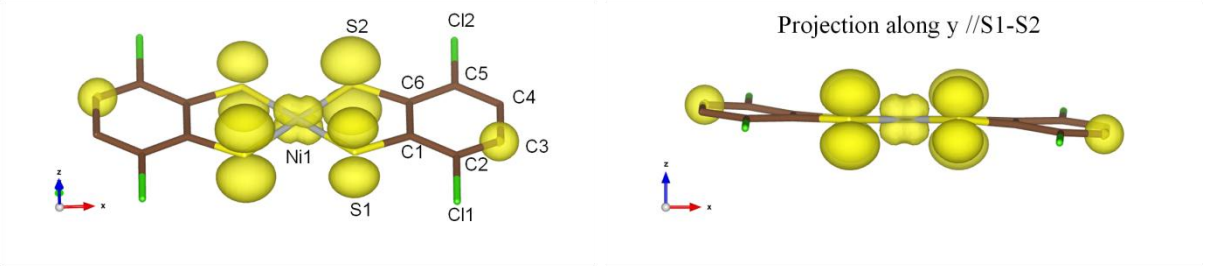
	Multipole parameters	Calculations BP86/VTZ [2]	
	outxzt	Mulliken	QTAIM
k Ni	1.25(6)		
k S	0.64(2)		
Ni1 2nd mono	0.397(12)	(Ni1) 0.423	0.426
1st mono	0.04		
4-pol zz	0.054541		
4-polxx-yy	0.090211		
16-pol z4	-0.097466		
16-p x2-y2	0.102329		
Ni2 2nd mono	0.404(10)	(Ni1) 0.423	0.426
1st mono	0.04		
4-pol zz	0.055582		
4-polxx-yy	0.091932		
16-pol z4	-0.099325		
16-p x2-y2	0.104282		
S1	0.097(12)	(S2) 0.115	0.109
4-pol zz	0.023255		
4-pol zx	0.026820		
4-pol zy	-0.007778		
4-polxx-yy	0.097064		
4-pol xy	0.023255		
S2	0.146(9)	(S3) 0.116	0.109
4-pol zz	0.051130		
4-pol zy	0.021824		
4-pol xx-yy	-0.002728		
S3	0.120(10)	(S2) 0.115	0.109
4-pol zz	0.042182		
4-pol zy	-0.018005		
4-pol xx-yy	-0.002251		
S4	0.103(12)	(S3) 0.116	0.109
4-pol zz	0.039493		
C3	0.030(7)		
C4	0		
C7	0.045		
C8	-0.034(9)		
C9	0.047(11)		
C10	0.012(7)		
Sum (Ni1+2(S1+S2+C3)	0.94(3)		
Sum (Ni2+2(S3+S4+C7+C8+C9+C10))	0.99(3)		
GOF	1.336		
Rw (|R-1 |)	0.129		

Local axes systems:

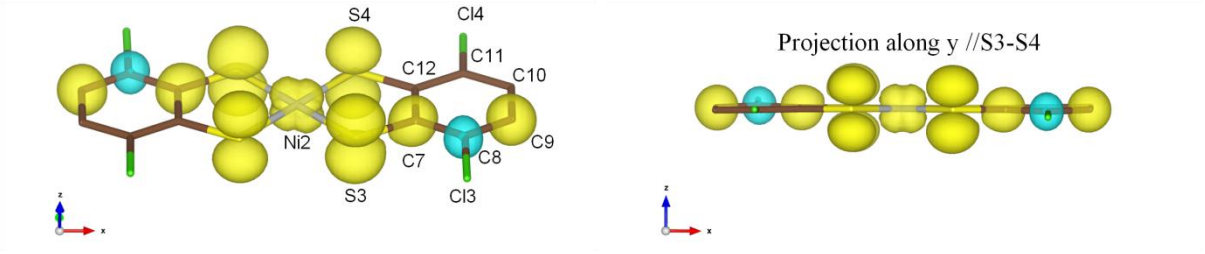
- centered on Ni1 : z ⊥ (Ni1-S1,Ni1-S2), y//(S1-S2), x⊥(y,z) , same for S1,S2

- centered on Ni2 : z ⊥ (Ni1-S3,Ni1-S4), y//(S3-S4), x⊥(y,z) , same for S3, S4

Molecule 1



Molecule 2



- spin populations for analogous atoms of nickel and sulphur in both molecules are comparable
- in both molecules one sulphur atom is more populated than another one
- obtained results are in agreement with preliminary theoretical ones