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## BACKGROUND

Rare earth metals (REMs) are known to form stable high coordination compounds (Coordination number 6 to 9) with hard Lewis bases. However, due to the similar chemical properties, the tendency and the mode of complexation of different REMs towards coordinating ligands is still a topic of intense research. Thus, understanding even the small structural variations of the REM complexes will be of great importance, especially in such fields where separation techniques are involved.

### HOW DO WE GET THE STRUCTURAL INFORMATION?

#### ❖ WE HAVE USED THE FOLLOWING TECHNIQUES

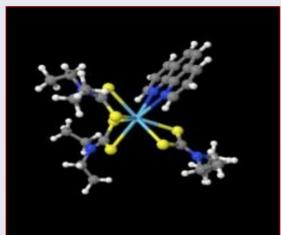
- ✓ <sup>13</sup>C and <sup>15</sup>N Solid State CP/MAS NMR,
- ✓ X-Ray Diffraction, and
- ✓ Preliminary DFT calculations with Amsterdam Density Functional (ADF) package [2].

### WHICH COMPLEXES HAVE BEEN STUDIED?

Six diamagnetic polycrystalline rare earth dialkyldithiocarbamates of the general formula [(Ln)<sub>2</sub>S<sub>2</sub>CNR<sub>2</sub>]<sub>3</sub> PHEN] (where Ln=La or Y, R=C<sub>2</sub>H<sub>5</sub>, C<sub>3</sub>H<sub>7</sub>, and i-C<sub>3</sub>H<sub>7</sub>) [1].

## STRUCTURAL VARIATION ?

“Rare earth complexes of dialkyldithiocarbamates and phenanthroline (3:1) ligands always crystallize in a monoclinic system with a space group P21/c” [1].



[Nd(S<sub>2</sub>CNEt<sub>2</sub>)<sub>3</sub>PHEN]

Crystal system: monoclinic  
Space Group: P21/c  
a/Å 16.917(4)  
b/Å 10.596(3)  
c/Å 18.649(5)  
̑/deg 96.759(4)

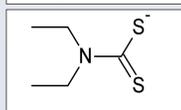
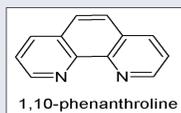
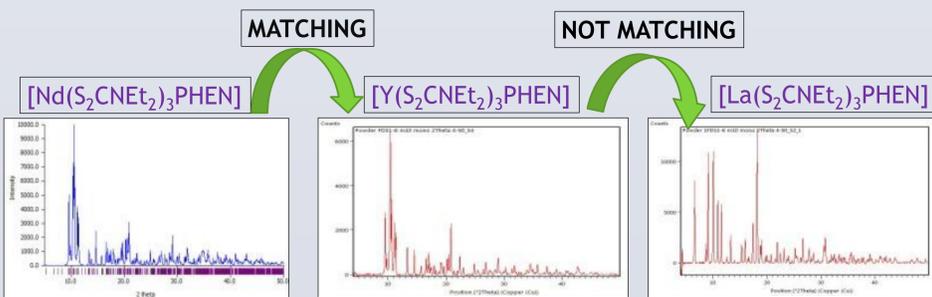


Fig. 1. Crystal Structure for Neodymium diethyldithiocarbamate [1].

### Comparative analysis of X-Ray diffraction powder pattern of polycrystalline Y and La diethyldithiocarbamate complexes



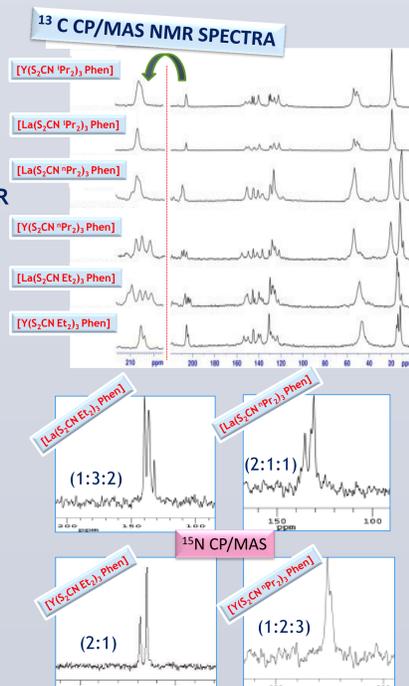
### Comparative analysis of solid state <sup>13</sup>C/<sup>15</sup>N CPMAS spectra of polycrystalline Y and La dithiocarbamate complexes

Table I: NMR Experimental Details

Nuclei	Resonance Freq. MHz	Spinning Freq. kHz	Pulse Length
<sup>1</sup> H	359.91	-	π/2- 5.0 us
<sup>13</sup> C	90.52	8.0-8.5	CT=3 ms
<sup>15</sup> N	36.48	4.0-5.0	CT=2.0-3.0 ms

TABLE II: <sup>13</sup>C and <sup>15</sup>N chemical shifts from CP/MAS NMR

Complexes	-C(S)-S	-N(R)-R
[La(S <sub>2</sub> CNEt <sub>2</sub> ) <sub>3</sub> Phen] (Acetonitrile)	207.81 206.84, 204.84 203.47 201.99 (1:2:1:1:1)	132.8, 137.1, 140.2 (1:3:2)
[La(S <sub>2</sub> CN <sup>n</sup> Pr <sub>2</sub> ) <sub>3</sub> Phen]	211.05, 209.33, 208.29, (1:3:2)	131.0, 132.5, 135.7 (2:1:1)
[La(S <sub>2</sub> CN <sup>i</sup> Pr <sub>2</sub> ) <sub>3</sub> Phen]	205.97, 205.37, (1:1)	149.2, 150.4, 155.0 (1:1:1)
[Y(S <sub>2</sub> CNEt <sub>2</sub> ) <sub>3</sub> Phen]	205.52, 204.03, (2:1)	137.3, 130.4 (2:1)
[Y(S <sub>2</sub> CN <sup>n</sup> Pr <sub>2</sub> ) <sub>3</sub> Phen]	209.72, 207.92, 205.38, (1:1.5:1)	123.8, 124.5, 126.0 (1:2:3)
[Y(S <sub>2</sub> CN <sup>i</sup> Pr <sub>2</sub> ) <sub>3</sub> Phen]	206.16	-



## COMPUTATIONAL DETAILS

### GEOMETRY OPTIMIZATIONS OF La AND Y COMPLEXES:

- Initial coordinates were taken from the single crystal x-ray data reported for the [Nd(S<sub>2</sub>CNEt<sub>2</sub>)<sub>3</sub>Phen] Ref.[1](see Table III)
- Delocalized internal coordinates
- Level of theory: BP/TZ2P
- Level of relativistic theory: Scalar ZORA.

### NMR CHEMICAL SHIFTS AND

#### SHIELDING CONSTANTNS:

- ❖ STO basis sets from the standard ADF basis set library

- ❖ TMS chemical shifts have been calculated

with the same level of theory for each basis set and used as the reference ( $\delta_{iso} = \sigma_{TMS} - \sigma_{iso}$ )

Table III: Measured bond angles and mean bond lengths before (#) and after geometry optimization(\*). Ln= Nd, Y or La. N = aromatic nitrogen atoms.

Atom Labels	Nd <sup>#</sup>	Nd <sup>*</sup>	Y <sup>*</sup>	La <sup>*</sup>
Bond Angles				
S-C9-S	118.4	118.6	118.2	119.9
S-C34-S	118.7	119.0	119.0	120.3
S-C33-S	119.0	119.5	119.2	120.5
N-Ln-N	63.1	62.7	64.9	60.2
Bond Lengths				
S-Ln	0.288	0.289	0.283	0.296
N-Ln	0.262	0.264	0.256	0.274

Table IV: <sup>13</sup>C isotropic shielding constants and chemical shifts (ppm) of <sup>13</sup>C (S-S-; integration 6.0; Relativistic- ZORA- all electron, [Y(S<sub>2</sub>CNEt<sub>2</sub>)<sub>3</sub>Phen]

Atom Label	PBE (TZ2P)	BLYP (TZ2P)	BP (DZP)	BP(TZP)	BP (TZ2P)	Expt					
	$\delta_{iso}$	$\sigma_{iso}$	$\delta_{iso}$	$\sigma_{iso}$	$\delta_{iso}$	$\delta_{iso}$					
C9	212.1	-24.27	216.8	-33.6	197.5	-3.0	210.6	-23.8	205.3	-24.0	205.52
C33	210.0	-22.15	214.5	-31.4	195.0	-0.4	208.4	-21.6	205.4	-24.1	204.03
C34	210.1	-22.24	215.3	-32.2	195.9	-1.3	208.4	-21.7	206.0	-24.8	(2:1)

Table V: <sup>13</sup>C isotropic shielding constants and chemical shifts (ppm) of <sup>13</sup>C (S)-S-; integration 6.0; Relativistic- ZORA - all electron, [La (S<sub>2</sub>CNEt<sub>2</sub>)<sub>3</sub>Phen]

Atom Label	PBE (TZ2P)	BP (DZP)	BP(TZP)	BP (TZ2P)	Expt				
	$\delta_{iso}$	$\sigma_{iso}$	$\delta_{iso}$	$\sigma_{iso}$	$\delta_{iso}$				
C9	210.8	-23.0	196.2	-1.6	208.9	-22.2	205.6	-24.3	207.81, 206.84
C33	209.4	-21.6	194.8	-0.2	207.5	-20.7	204.1	-22.8	204.84, 203.47
C34	210.2	-22.3	195.4	-0.9	208.2	-21.4	204.9	-23.6	201.99 (1:2:1:1:1)

## SUMMARY

- ✓ Comparative analysis of XRD Powder Patterns and solid state <sup>13</sup>C/<sup>15</sup>N CPMAS spectra of polycrystalline Yttrium and Lanthanum diethyldithiocarbamate complexes shows the presence of significant differences, indicating structural variations of these two complexes. Matching XRD pattern indicates that Yttrium complex adopts the same crystal structure as that of Neodymium (P21/c). However, observed five <sup>13</sup>C resonance peaks (1:2:1:1:1) and three <sup>15</sup>N resonance peaks (1:3:2) for lanthanum complex clearly suggests that it has two molecules in the unit cell. The structural variation of La complex is also supported from the XRD pattern.
- ✓ Results of preliminary DFT calculations of <sup>13</sup>C NMR chemical shifts (ppm) at BP/TZ2P level of theory are close to the experimental values. Again, bond angles and bond lengths of the calculated structure for Y complex does not vary much when compared to La complex (Table III).

## REFERENCES

- [1] Regulacio MD, Tomson N, Stoll SL. *Chem. Mater*, 2005, 17(12), 3114-3121
- [2] Te Velde G, Bickelhaupt FM, Baerends EJ, et al. *J. Comp. Chem.*, 2001, 22(9), 931-967.

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