Experimental report

24/01/2024

Proposal: DIR-292 **Council:** 4/2023

Title: Structural characterization of Ca(II)-N2 Complexes

Research area: Chemistry

This proposal is a new proposal

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Samples: C57 H69 Ca3 I3 N14 O3 · x moléculas de CDCl3/Hexano

Instrument	Requested days	Allocated days	From	To
D19	8	6	18/09/2023	19/09/2023
			22/09/2023	23/09/2023
			20/11/2023	26/11/2023

Abstract:

Dinitrogen activation by d-block metals has been well developed over the last decades and suggests that d orbitals play an important role in weakening the triple bond. However, it has been proved that their contribution is not an absolute requirement. Some of these metals are scarce and expensive, so one challenge is finding other abundant metal compounds capable of activating the N2 molecule. Here we would like to examine how the N2 molecule binds to Ca(II) atoms, which could initiate its activation.

DIR-292 experimental report.

Structural characterization of Ca(II)-N2 Complexes.

After a first measurement attempt on 18 September 2023, having verified that the sample did not diffract sufficiently, it was decided to cancel the experiment and delay it until we could grow better quality crystals. Finally, we managed to crystallise crystals of adequate quality and size and the measurement was performed on 20 November 2023.

The crystal was wrapped in aluminium foil, to avoid degradation by contact with the glue, and stacked on a 1 mm diameter vanadium pin. A search of the UB matrix was performed and the triclinic cell was found to be 14.3 14.5 21.8 85.99 85.77 64.7 at RT, which matches the X-ray measurements. The measurement was made at 80K with a wavelength of 1.45Å. It consisted of ω-scans with a step of 0.07º at different values of χ and ϕ, to cover as much of the reciprocal space as possible, almost completely covering half of the limit sphere. The images were processed with the D19 specific software retreat and abscan. With this treatment, we obtained an hkl file with which we obtained the structural model using JANA2006. The model and crystallographic table of the measurement are detailed below.

Table 1. Crystallographic and experimental data of compound 1, measured on the single crystal neutron diffractometer D19.

Chemical formula	$C_{60}H_{71}Ca_3Cl_9D_3I_3LiN_{12}O_4$	T, K	80
M	1857.3	ρ_{calc}, mg m^{-3}	1.6216
Z	2	λ, Å	1.45947 (1)
Space group	*P* -1	μ, mm^{-1}	0.019
a, Å	13.9763 (4)	R_1, I > 2σ(I) (all)	0.0631 (0.0744)
b, Å	14.1203 (3)	wR_2, I > 2σ(I) (all)	0.0971 (0.1024)
c, Å	21.3905 (5)	Absorption Correction	Numerical
α, º	85.84(15)	Independent reflections	11797
β, º	84.852(14)		
γ, º	65.018(14)		
V, Å^3	3808.21 (17)		

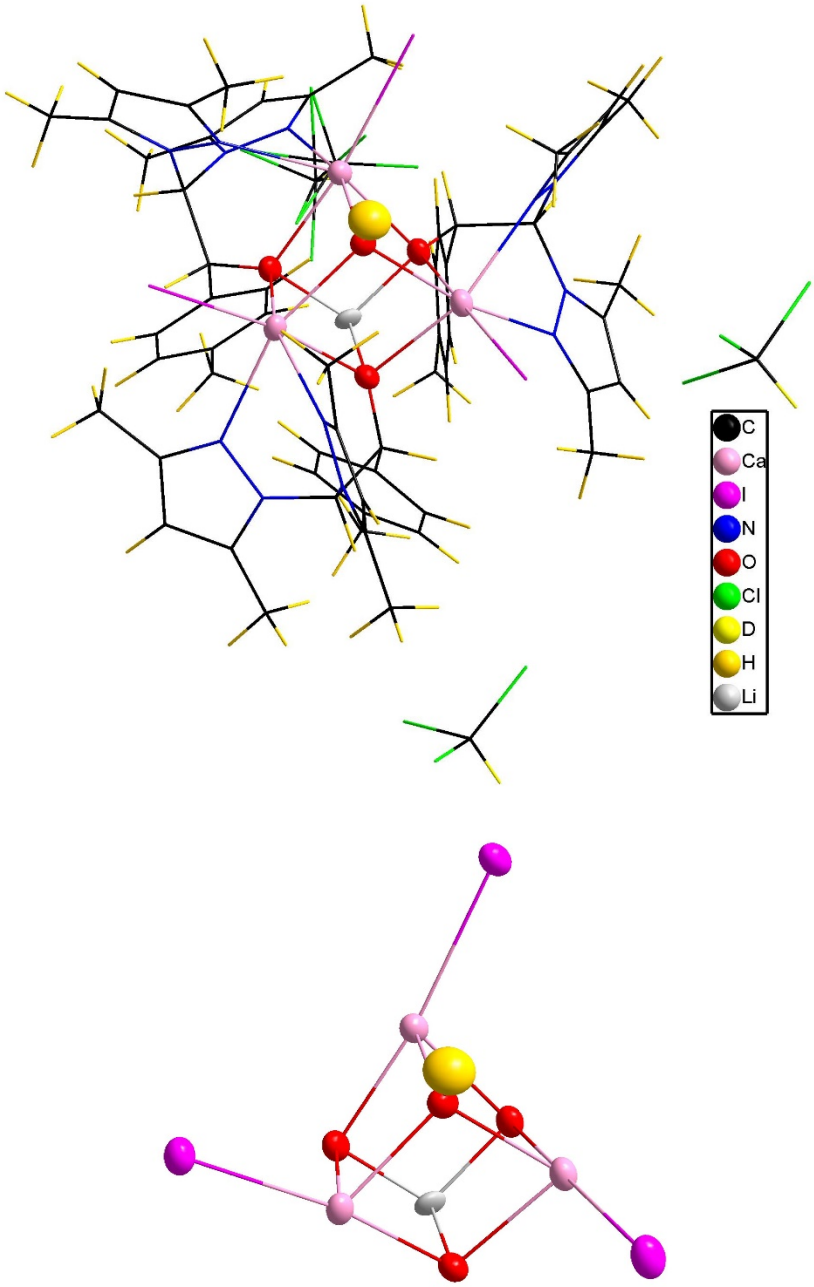

Figure 1. **Top**. Structural model refined with single crystal neutron data at 80 K. **Bottom**. Detail of the cage where the Li atom (represented in grey) is coordinated to three oxygen atoms (represented in red).

As can be seen in the model, the N_2 molecule that was intuited from previous X-ray measurements of smaller crystals was not trapped. Unfortunately, variations in the synthesis made to obtain larger crystals between the first measurement attempt in September and the final measurement in December resulted in a phase in which a Li is coordinated in place of the N_2 molecule. This result is interesting and we are already working on publishing the results, however we have also learned which elements of the synthesis led to the introduction of the Li, so we are in a position to synthesise the good phase with the N_2 molecule. Given that, we will apply for an extension of the present experiment in the next round of proposals.