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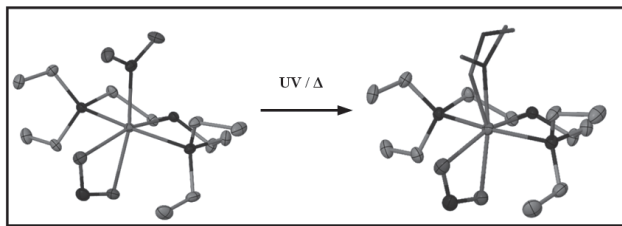
Acta Cryst. (2011) A67, C700**Thermal and photocrystallographic studies on a nickel-nitro complex**

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The technique of time-resolved crystallography has attracted much interest in recent years, as a result of rapid technological advancements in the field. These methods introduce the “fourth dimension” of time into the crystallographic experiment, allowing the structures of short-lived and metastable species to be determined [1].

In this work, nitro-(η^1 -NO₂) to nitrito-(η^1 -ONO) linkage isomerisation in the complex [Ni(Et₄dien)(NO₂)₂] (Et₄dien = N,N,N',N'-tetraethyldiethylenetriamine) has been studied using time-resolved crystallographic techniques. Significant levels of conversion are induced in the single-crystal when the complex is excited both photochemically and thermally. 86% conversion to the metastable nitrito-(η^1 -ONO) linkage isomer is achieved following irradiation with UV light, and a maximum 42% conversion is thermally induced when variable temperature studies are conducted between 100 K and 370 K.

This is the first crystallographic study to report both thermal and photochemical excitation of the nitrite ligand in the same system.



[1] P. Coppens, I.I. Vorontsov, T. Graber, *Acta Cryst. A* **2005**, 61, 162.

Keywords: photocrystallography, photoactivation, nitrite

MS80.P05

Acta Cryst. (2011) A67, C700**Crystal structure and luminescence properties of lanthanide-containing organic complexes**

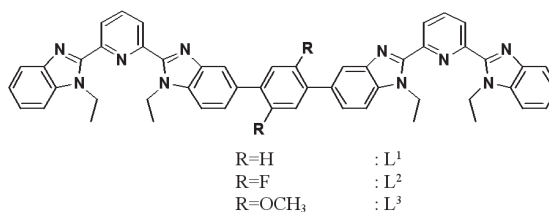
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In order to rationalize and design luminescent lanthanide-containing organic complexes, the central phenyl ring separating 2,6-bis(benzimidazol-2-yl)pyridine binding units in the bis-tridentate model ligands L¹-L³ were substituted with neutral (R=H, L¹), electro-attracting (R=F, L²) or electro-donating (R=OCH₃, L³) groups. Reaction of these ligands with Ln(hfac)₃ salts give poorly soluble dinuclear single strand complexes [Ln₂Lⁱ(hfac)₃] (i=1-3).

X-Ray single crystal structure analyses revealed that the stepwise connection of bulkier substituent onto the central phenyl ring (R=H < R=F ~ R=OCH₃) increases the inter-annular phenyl-benzimidazole interplanar angles (25° < α < 54°). This structural feature is expected to affect the HOMO-LUMO gap in the various complexes (as exemplified by TD-DFT calculations for the ligands in gas-phase).

Solid state photophysical properties on [Eu₂Lⁱ(hfac)₃] (i=1-3)

revealed that the ligand-to-metal energy transfer is significantly affected by the choice of the substituent and we conclude that the electro-attracting substituent F is the best candidate simultaneously matching structural and solution properties, and photophysical characteristics.



Keywords: lanthanide, luminescence, polyaromatic ligands

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Acta Cryst. (2011) A67, C700-C701**Flux growth of piezoelectric single-crystals from the SiO₂-GeO₂ binary diagram**

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Nowadays, synthetic α -quartz is still the most extensively used piezoelectric material. Its zero temperature coefficients cut (AT-cut) and its low acoustic loss are exploited in Surface Acoustic Waves devices (filters, oscillators, resonators...). However, its piezoelectric properties are limited in temperature due to its transition towards the non piezoelectric β -quartz phase, which occurs at 573°C. Besides, its electromechanical coupling coefficient is low (k=11%) considering those obtained by PZT ceramics (k=60-90%).

In order to increase the electromechanical coupling coefficient and the thermal stability domain, the solid-solution between SiO₂ and GeO₂, a quartz analog, was investigated. The main interest of GeO₂ is its high structural distortion: in theory, as regards to previous studies on the α -quartz homeotype family, its piezoelectric performances, linked to distortion, should be three times higher. Furthermore, no α/β -quartz phase transition appears in α -GeO₂. Both parts of the Ge_{1-x}Si_xO₂ solid-solution were studied. The rich SiO₂-content compositions where some Si⁴⁺-substitution by Ge⁴⁺ delay the α/β -quartz phase transition and the rich GeO₂-content compositions where some Ge⁴⁺-substitution by Si⁴⁺ atoms stabilize the α -quartz phase of GeO₂ (metastable at ambient temperature). The increase of the structural distortion in germanium-substituted SiO₂ compositions should also improve their piezoelectric performances.

Single-crystals from both side of the binary SiO₂-GeO₂ diagram have already been synthesized by the hydrothermal method. However, the use of water as growth medium favors the formation of water inclusions in crystals. These inclusions were avoided by the use of a novel way to grow single-crystal of this system: the high-temperature flux growth technique. The growth process was optimized to enlarge the transparent, colorless and well-faceted crystals obtained. Millimeter-size flux-grown Ge_{1-x}Si_xO₂ single-crystals, crystallizing in the trigonal space group P3₁21 or P3₂21, were grown by spontaneous nucleation with the slow cooling method. Different macroscopic morphologies, going from pseudo-cubic shape to hexagonal prism-like shape, were observed depending on the nature of the flux, the substitution content and the sursaturation rate.