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Preparation, crystal structure and luminescent properties of a Sc(III) complex with a pyrazole substituted β-diketone

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A new neutral ternary scandium complex, Sc*L*$_3$, in which H*L* is 1,3-bis-(1,3-dimethyl-1H-pyrazol-4-yl)-1,3-propanedione, has been synthesized. The molecular structure of the complex was determined by single crystal X-ray diffraction. UV-absorption, excitation and emission spectra of the title compound were investigated. Under UV-light the complex demonstrates bright blue molecular luminescence (λ_{max} = 450 nm).

Scandium / 1.3-Diketones / Complexes / X-ray structure / Luminescence

Introduction

Lanthanide β-diketonate complexes have been extensively studied as laser materials components [1], for light-emitting diodes (OLED) [2], fluorescent dyes [3] and non-linear materials for optical devices [4]. Much less attention has been paid to β-diketonate complexes of other elements of group III of the periodic table (Sc, Y). For example, only a few crystal structures of simple scandium diketonates have been reported in the literature up to date [5,6].

Due to our continuous interest in the synthesis and application of novel pyrazole-based diketones, we wish to report here about the synthesis and solid-state structure of a scandium complex with 1,3-bis(1,3-dimethyl-1*H*-pyrazol-4-yl)-1,3-propanedione (H*L*).

Experimental

The ligand was synthesized by a known method [7]. All the other reagents were purchased from Aldrich and used without further purification. Elemental analysis was performed on an Elementar CHNO(S) analyzer. UV-Vis absorption spectra were recorded on a Perkin-Elmer Lambda 45 instrument. Solid-state luminescent spectra were measured on a Perkin-Elmer SL-45 spectrofluorimeter in quartz tubes. Determination of Sc was performed in the Laboratory of Microanalysis of the A.N. Nesmeyanov Institute of Organoelement Compounds of the RAS.

*Synthesis of **1** [ScL_3] and solvate **2***

A solution of $ScCl_3$ was prepared by treatment of Sc_2O_3 (2 g, 14.5 mmol) with 8 ml of pure conc. HCl, evaporation of the reaction mass to dryness and dissolution of the residue in deionized water in a volumetric flask. The overall volume was brought to 20 ml.

1.15 g (4.35 mmol) of H*L* was dissolved in 15 ml of ethanol (*Et*OH). To this solution 1 ml (1.45 mmol) of $ScCl_3$ solution was added under stirring and pH was adjusted to 9 by careful addition of a 25% aqueous ammonia solution (Fig. 1). The reaction mixture was incubated at 60ºC in a sealed flask for 2 h (a thick white precipitate was formed) and then it was stirred overnight at room temperature. The solvent was removed under reduced pressure. The residue was transferred onto a sintered glass filter and washed successively with 10 ml of water, 10 ml of 30% aqueous ethanol, 10 ml of ether and finally with 10 ml of CH_2Cl_2 and dried *in vacuo*. The yield of the colorless crystalline powder was 0.65 g (54%).

A sample for chemical analysis was recrystallized from a DMSO-CH_2Cl_2 mixture, washed with CH_2Cl_2 and dried to constant weight under reduced pressure ($1\cdot10^{-2}$ Torr).

Anal. for $C_{39}H_{45}N_{12}O_6Sc$ (**1**): calcd. C 56.93, H 5.51, N, 20.43, Sc 5.46; found: C 57.07, H 5.79, N 20.67, Sc 5.51.

Single crystals of solvate **2,** suitable for X-ray diffraction, were obtained by slow diffusion of acetonitrile (*Me*CN) vapor onto a saturated solution of **1** in DMSO at room temperature. The crystals are not stable in air at room temperature and easily lose the solvent with crystal degradation.

Table 1 Crystal data and structure refinement parameters for **2**.

Empirical formula	$C_{45}H_{54}N_{15}O_6Sc$	D_{calc}, Mg·m^{-3}	1.327
Formula weight	945.99	μ, cm^{-1}	2.2
T, K	100(2)	F(000)	1494
Space group	$R\bar{3}$	$2\theta_{max}$, °	57
Z (Z')	3 (1/3)	Reflections collected (R_{int})	6836 (0.0261)
Crystal system	Trigonal	Independent reflections	3873
a, Å	19.1881(14)	Observed reflections with $I > 2\sigma(I)$	3406
b, Å	19.1881(14)	Number of parameters	208
c, Å	11.1360(8)	$R1$	0.0327
V, Å^3	3550.8(4)	w$R2$	0.0771
GOF	1.034	Largest diff. peak and hole, e·Å^{-3}	0.287/-0.265

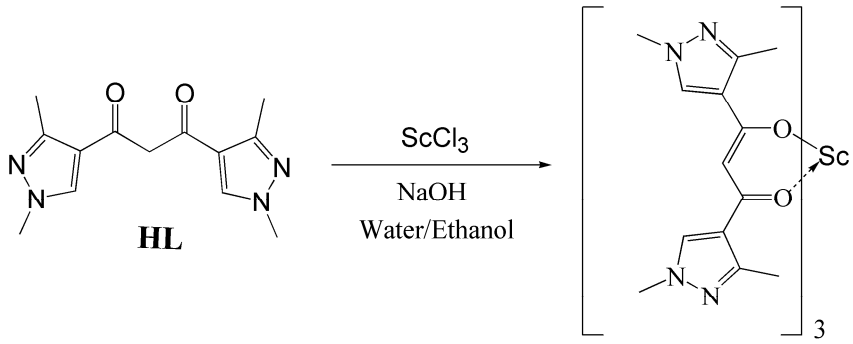

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Fig. 1 Preparation of **1**.

Crystal data

From the *Me*CN-DMSO mixture rhombohedral colorless crystals of the solvate **1**·3*Me*CN (**2**) were obtained. Crystal data and structure refinement parameters for **2** are summarized in Table 1. Selected bond lengths and angles for this compound are listed in Tables 2 and 3.

The diffraction data were collected on a Bruker SMART APEX II CCD diffractometer [λ(Mo $K\alpha$) = 0.071072 nm, ω-scans]. The substantial redundancy in data allowed an empirical absorption correction to be performed with SADABS [8,9], using multiple measurements of equivalent reflections. The structures were solved by direct methods and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. All calculations were performed with the SHELXTL software package [9]. CCDC № 917057 contains the supplementary crystallographic data for **2**. These data can be obtained free of charge from the Cambridge Crystallographic Data via www.ccdc.cam.ac.uk/data_request/cif.

Results and discussion

Synthesis

We have recently described a simple approach to prepare ternary lanthanide complexes with pyrazole substituted 1,3-diketones and 1,10-phenantroline [10]. Practically the same method was used for the preparation of ScL_3, but because the coordination number of scandium is equal to 6, no additional ligands were needed to obtain a neutral complex:

Due to the relatively low solubility in aqueous ethanol and organic solvents like *Me*CN or CH_2Cl_2, the complex **1** could be separated from unreacted ligand and inorganic by-products by filtration and washing with water. After drying at 50°C (10-2 Torr), compound **1** was obtained free of solvent.

Molecular structure

The coordination polyhedron of the six-fold coordinated Sc atom in compound **2** is a distorted trigonal antiprism. The Sc-O bond distances are in the range of 2.078(1)-2.095(1) Å (practically the same range of Sc-O(1-6) bond distances was found for the complex Sc(*tfacac*)$_3$ [6]). No hydrogen bonds were detected in the structure of **2**. The molecular and crystal structures of **2** are shown in Figs. 2 and 3, respectively.

In the presence of *Et*OH another type of solvate was formed. Several types of crystal with different ratios of *Et*OH and *Me*CN (up to 2 moles of *Et*OH and 1 mole *Me*CN per 1 mole of **1**) were separated, but the solvent molecules were strongly disordered in all cases and, unfortunately, reliable structural data were not obtained.

Table 2 Selected bond lengths (Å) and angles (°) for **2**.

Bond	Length, Å	Angle	Degrees
Sc(1)-O(1)	2.079(1)	O(1)-Sc(1)-O(2)	81.24(5)
Sc(1)-O(2)	2.086(1)	O(3)-Sc(1)-O(4)	81.24(6)
Sc(1)-O(3)	2.079(2)	O(5)-Sc(1)-O(6)	81.24(6)
Sc(1)-O(4)	2.086(2)	Sc(1)-O(1)-C(1)	133.0(1)
Sc(1)-O(5)	2.079(1)	Sc(1)-O(2)-C(3)	132.9(1)
Sc(1)-O(6)	2.086(1)	C(1)-C(2)-C(3)	123.6(2)

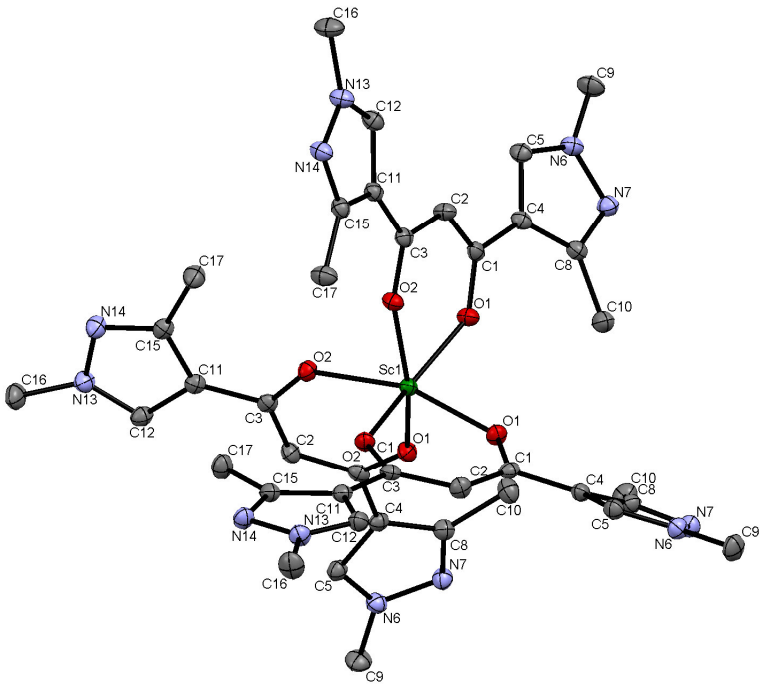

Fig. 2 Molecular structure of **1** from the structure refinement of solvate **2**. The thermal ellipsoids are shown at the 50% probability level. Atoms color: Sc (green), N (blue), O (red), C (grey). The hydrogen atoms have been omitted for clarity.

Nevertheless, for the solvate **1**·*Et*OH·*Me*CN a monoclinic structure type (space group $P2_1/n$, cell parameters: a = 11.8292(6) Å, b = 17.3915(9) Å, c = 21.7841(11) Å, β = 93.0564(11)°) was determinated.

Formation of different polymorphic forms of scandium diketonates by crystallization from various solvents has previously been reported in the literature and seems to be a common phenomenon for this type of compound. For example, two crystal forms of tris(dibenzoylmethanato)scandium(III) were reported in [11]. The monoclinic ($P2_1/c$) and triclinic (P-1) forms were obtained by crystallization of the complex from different solvents.

Photophysical studies

The UV-Vis absorption spectra of H*L* (curve 1) and complex **1** (curve 2) in acetonitrile (solutions with concentrations of $4.4\cdot10^{-5}$ and $1.7\cdot10^{-5}$ M, respectively, were used) are shown in Fig. 4.

Complex **1** demonstrated high UV-light absorption in a wide spectral range (200-380 nm). The absorption maxima in the ScL_3 spectrum are red-shifted with respect to the spectrum of the free ligand and characterized by a high extinction coefficient (26470 at 350 nm). The excitation spectrum (curve 1) of a ScL_3 crystal (λ_{em} = 430 nm) and the emission spectrum of **1** in crystals (curve 2) are shown in Fig. 5. Since Sc^{3+} has no *f*-electrons, only ligand-centered luminescence could be observed. The bright blue emission is characterized by a relatively wide band of molecular luminescence with a maximum at 450 nm. No phosphorescence was detected at room temperature.

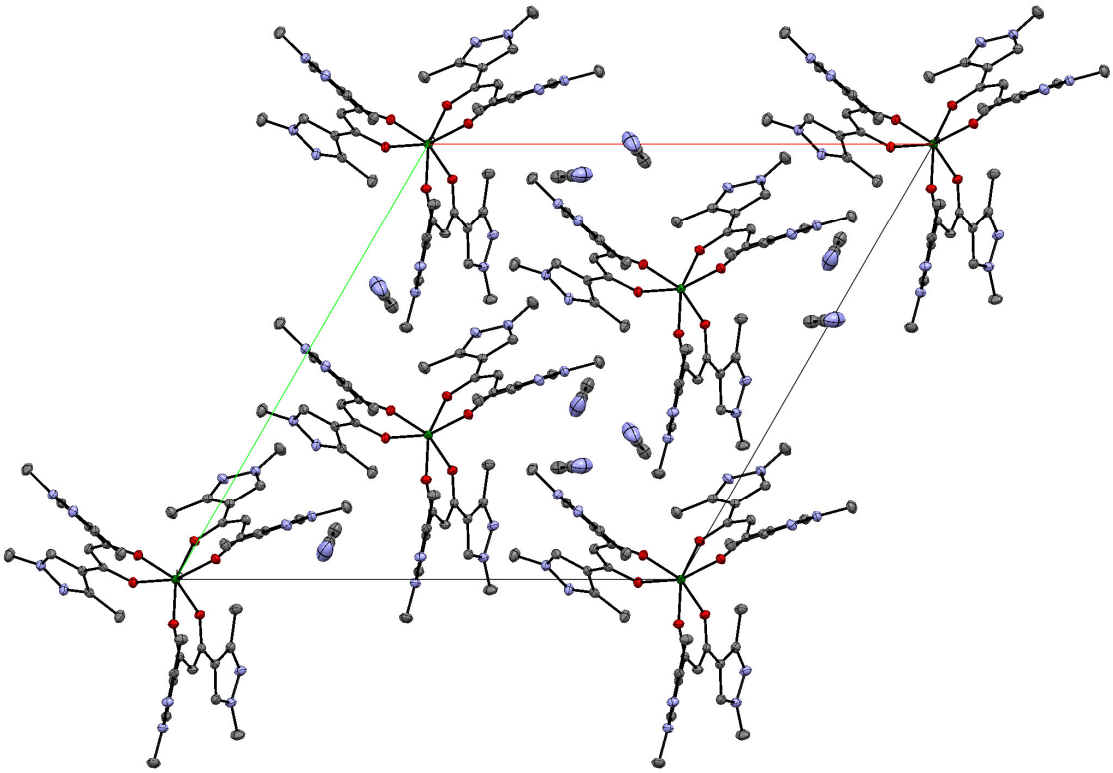

Fig. 3 View along the *c*-axis on the crystal structure of **2**. Atoms color: Sc (green), N (blue), O (red), C (grey). The hydrogen atoms have been omitted for clarity.

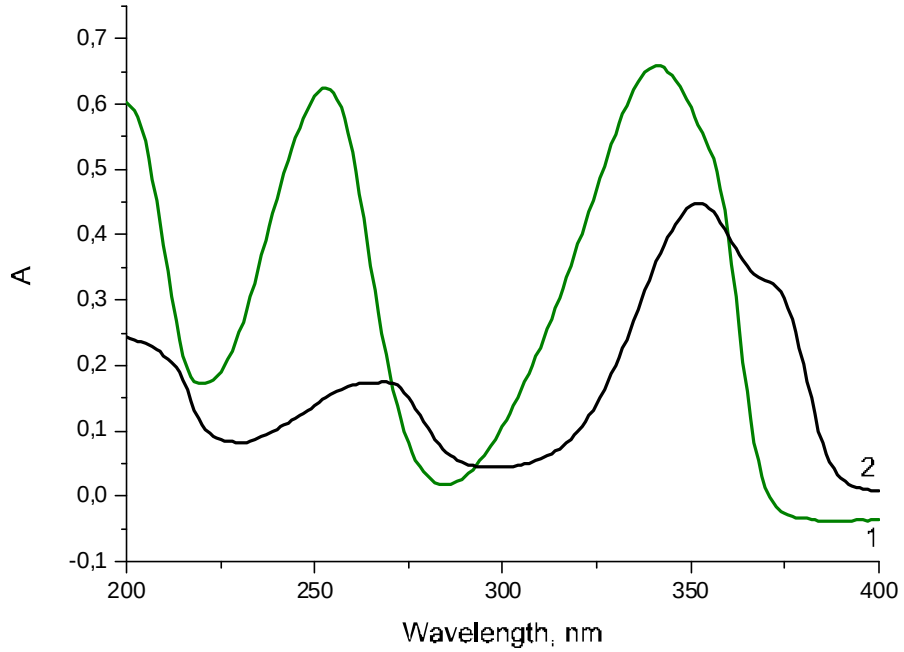

Fig. 4 UV-Vis absorption spectra of H*L* (1, green line) and complex **1** (2, black line) in acetonitrile.

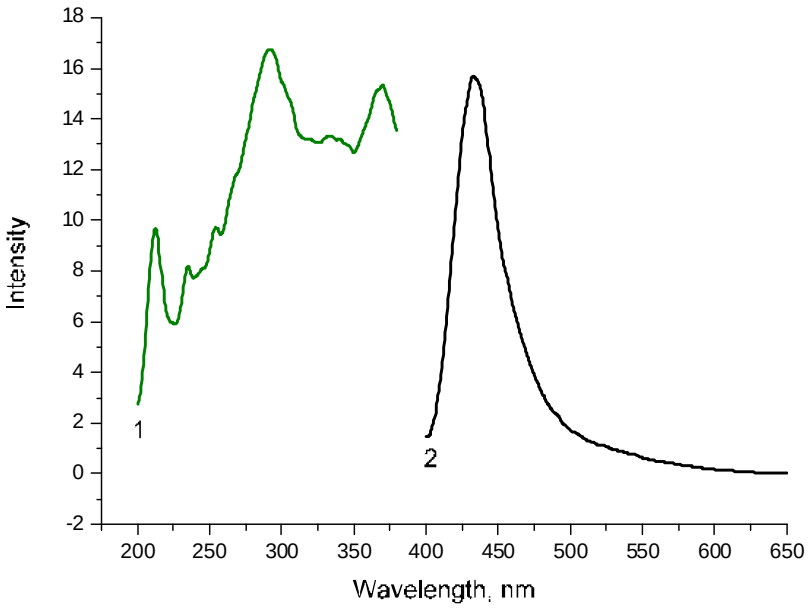

Fig. 5 Excitation spectrum (1, green line) of a ScL_3 crystal (λ_{em} = 430 nm) and normalized emission (λ_{ex} = 360 nm) spectrum of **1** in crystals (2, black line).

Acknowledgements

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