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Crystal Structure and Optical Properties of a Lanthanum(III) Complex of the Solvatochromic Dye "Nile Red"

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A carbethoxy derivative of the push-pull chromophore benzo[*a*]phenoxazin-5-one (Nile Red) forms chelate complexes of the trivalent lanthanide ions that are stable in coordinating solvents with a bathochromic shift of the intense charge-transfer band in the Nile Red chromophore as a result. The complex formation results in quenching of the fluorescence from the free Nile Red ligand. Single crystals of a lanthanum(III) complex have been grown and the X-ray crystal structure showed that two Nile Red ligands are coordinated to the metal centre.

Introduction

The benzo[*a*]phenoxazine compound Nile Red (nr) is a widely used fluorescent laser dye (Figure 1). The intense absorption band ($\varepsilon_{\max} \approx 35000\ \mathrm{cm^{-1}\,M^{-1}}$), located in the VIS range,[1] displays some charge transfer character in which electron density is moved from the diethylamino group to the carbonyl group, and nr is, accordingly, often referred to as a so-called push-pull chromophore. The positions of the absorption and emission bands are highly sensitive to the nature of the solvent (polarity and hydrogen-bond acidity), and the absorption maximum ranges from 484 nm in pentane to 629 nm in trifluoroacetic acid.[2] This solvatochromic effect has its origin in the fact that the molecule in the first excited singlet state is geometrically distorted with a significantly higher dipole moment than in the ground state. Exhibiting such twisted intramolecular charge transfer (TICT) properties nr has thus been used extensively as a polarity probe in chemical and biophysical environments.[3] Moreover, Verhoeven found recently that nr was able to sensitize a metal-centred NIR emission from the complexes [Ln(fod)$_3$(nr)] (Ln = Er or Yb, fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dione) in benzene solution.[4] However, complex formation between the Lewis acids [Ln(fod)$_3$] and nr, that occurs through the carbonyl oxygen atom in nr, is weak and does not take place in more coordinating solvents such as acetonitrile (MeCN). In an attempt to overcome this obstacle we have, during our investigations in this field,[5] used a derivative of nr, namely nr-C(O)OEt shown in Figure 1. The attached carbethoxy group makes the formation of a chelate metal complex [Ln^{III}{nr-C(O)OEt}] possible, resulting in enhanced stability of the metal complexes of nr-C(O)OEt. We present here results that show that nr-C(O)OEt forms complexes with lanthanide(III) (Ln^{III}) ions in coordinating solvents. Single crystals of a lanthanum(III) complex of nr-C(O)OEt have been grown, and the crystal structure of this complex has been determined. Despite the fact that nr has been widely used as a polarity probe and that the electronic structure of nr has been subject to numerous theoretical studies,[6] this contribution describes the first example of a crystal structure determination of a compound that includes an nr chromophore.

Results and Discussion

The synthesis of nr-C(O)OEt has been described by Meng,[7] who prepared a whole series of nr derivatives. From an MeCN solution of nr-C(O)OEt and La(OSO$_2$CF$_3$)$_3$, single crystals of [La{nr-C(O)OEt}$_2$(OSO$_2$CF$_3$)$_3$(OH$_2$)$_2$]·H$_2$O (**1**) were grown. Figure 2 shows the molecular structure of **1**. The lanthanum(III) centre in **1** is coordinated by two molecules of nr-C(O)OEt (each bidentately coordinated as shown in Figure 1), two water molecules, and three triflate anions that are monodentately bound through the oxygen atoms. The coordination geometry is best described as tricapped trigonal prismatic. The La–O bond lengths are normal for these types of ligators. Of special note is the bonding geometry around the aliphatic, tertiary N1 and N3 atom. Firstly, the geometry is close to trigonal planar, and the C–N–C angles range from 115° to 122°, and the C–C8–N1–C and C–C31–N3–C dihedral angles range from 2° to 6° and from –170° to –178°, respectively. Secondly, the N1–C8 and N3–C31 bond lengths of 1.353(3) and 1.330(3) Å, respectively, are significantly shorter than expected for a N(sp^3)–C(sp^2) bond (1.467(2) Å in 4-aminobenzonitrile hydrochloride).[8] This can be rationalized if we take the ionic

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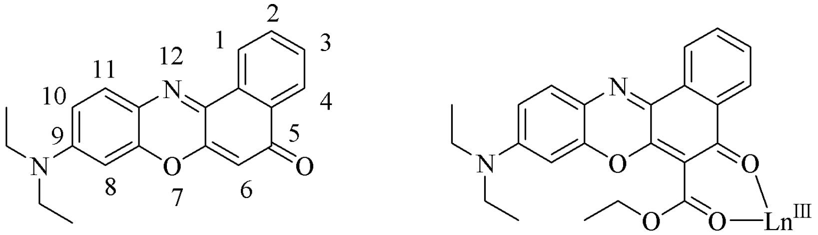

9-diethylamino-5*H*-benzo[*a*]-phenoxazin-5-one, Nile Red (nr)

[Ln^{III}{nr-C(O)OEt}]

Figure 1. Structure of the ligands nr and nr-C(O)OEt; the latter ligand is chelated to a lanthanide(III) ion (Ln^{III}).

resonance structure shown in Figure 3 into account. Here, the lone pairs of electrons on N1 and N3 reside in a pure p orbital which is conjugated with the aromatic ring; this results in an increased order of the N1–C8 and N3–C31 bond and delocalization of a negative charge on the β-keto ester group, as shown in Figure 3. Similar behaviour was seen in other acceptor-substituted aromatic amines such as 4-(dimethylamino)benzonitrile[9] and 4-nitroso-*N*,*N*-diethylaniline[10] in which the analogous C–N bond length was 1.366(2) and 1.358(4) Å, respectively. Han et al. calculated, by density functional methods, the bond lengths of nr in the ground state and the first excited singlet state both in the gas phase and in H_2O solution.[6b] It is worth noting that the bond lengths of the nr-C(O)OEt ligand in **1** agree (within 0.01 Å) with the calculated bond lengths of nr in the ground state in H_2O solution. With regard to other metal complexes of nr, it should be noted in this context that Ghedini isolated the cyclometalated, square-planar complexes of the type [Pd(nr)(acac)] (acac = acetylacetonate or derivatives thereof) in which the nr ligand supposedly bidentately coordinates through the N12 and deprotonated C1 atoms (the atom numbering is taken from Figure 1).[11] No crystal structures were, however, reported.

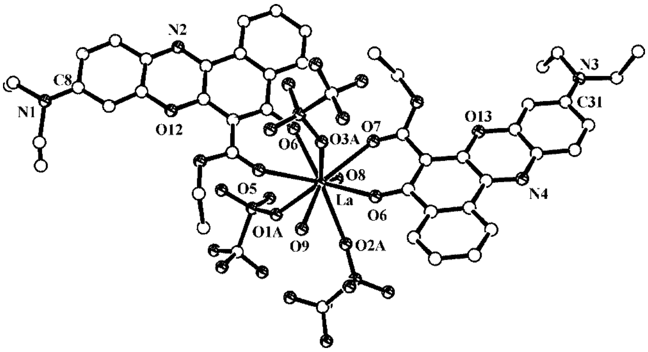

Figure 2. Molecular structure of the complex [La{nr-C(O)-OEt}$_2$(OSO$_2$CF$_3$)$_3$(OH$_2$)$_2$] with the hydrogen atoms omitted for clarity. The thermal ellipsoids are shown at the 50% probability. Ranges of bond lengths: La–O(triflate) 2.5623(16)–2.5985(16) Å, La–O(water) 2.5331(15)–2.5903(16) Å, La–O{nr-C(O)OEt} 2.4482(15)–2.5507(15) Å.

For the recording of the ^{1}H NMR spectra excess La(CF$_3$SO$_3$)$_3$ was added to an acetonitrile solution of nr-C(O)OEt in order to ensure that all nr-C(O)OEt was complexed. In the ^{1}H NMR spectrum of such a solution there are no peaks originating from free nr-C(O)OEt, and only one type of complexed nr-C(O)OEt is seen. The chemical shift values (δ) for complexed and free nr-C(O)OEt are shown in Table 1. It should be noted that the chemical shifts move downfield on complexation owing to the electron-withdrawing inductive effect of the metal ion, with the exception of those for 2-H, 3-H, and 4-H. The excess La(CF$_3$SO$_3$)$_3$ in the solution favours a 1:1 stoichiometry for La/nr-C(O)OEt, but it is worth noting that the crystals that separate out from the solution after long-term storage have a stoichiometry of 1:2.

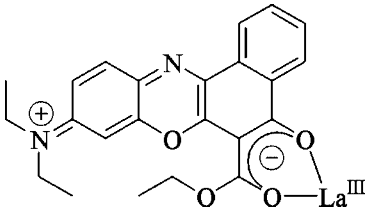

Figure 3. A resonance form of a lanthanum(III) chelate complex of nr-C(O)OEt.

Table 1. Chemical shift (δ/ppm) assignment of the ^{1}H NMR spectra of nr-C(O)OEt and [La^{III}{nr-C(O)OEt}] in CD$_3$CN at 298 K.

Nuclei	nr-C(O)OEt	La{nr-C(O)OEt}
N(CH$_2$C*H*$_3$)$_2$	1.21	1.40
OCH$_2$C*H*$_3$	1.41	1.52
N(C*H*$_2$CH$_3$)$_2$	3.48	3.73
OC*H*$_2$CH$_3$	4.45	4.65
1-H	8.19	8.38[a]
2-H	7.68	7.62
3-H	7.78	7.62
4-H	8.57	8.28[a]
8-H	6.55	6.59
10-H	6.83	7.38
11-H	7.61	7.81

[a] May be interchanged.

Stužka et al.[12] studied the IR spectra of various substituted benzo[*a*]phenoxazine compounds, and on the basis of that work, we assign the bands at 1640 and 1733 cm^{-1} in the IR spectrum of nr-C(O)OEt as carbonyl vibrations in the keto and ester groups, respectively. An IR spectrum of a solid with the formula [La{nr-C(O)OEt}$_3$](CF$_3$SO$_3$)$_3$·3H$_2$O (**2**) shows that metal complexation to the ester carbonyl oxygen atom results, in accordance with the resonance form in Figure 3, in a significant decrease in the ester carbonyl stretching frequency; this band appears as a shoulder (at $\tilde{\nu}$ = 1694 cm^{-1}) on the other (keto) carbonyl vibrational band at 1658 cm^{-1}.

The optical spectra of nr-C(O)OEt and its lanthanum(III) complex in solution can be seen in Figure 4. The pink colour of a MeCN solution of nr-C(O)OEt (λ_{abs}^{max} = 553 nm) changes to blue (λ_{abs}^{max} = 622 nm) upon addition of $La(CF_3SO_3)_3$. This bathochromic shift of the charge-transfer band is a result of the interaction between the electron-rich carbonyl group and the electron-withdrawing lanthanum(III) ion that lowers the diethylamino to carbonyl oxygen charge-transfer energy. A similar behaviour with other Ln^{III} ions and in other solvents is observed. With regard to the luminescence properties, solutions of nr-C(O)OEt display strong fluorescence with the emission maximum in MeCN located at λ_{em}^{max} = 627 nm (λ_{ex}^{max} = 553 nm). Addition of $La(CF_3SO_3)_3$ reduces the fluorescence intensity to about 10% of the original, and the emission maximum shifts to λ_{em}^{max} = 654 nm. Earlier studies of nr[13] have shown that the fluorescence lifetime and quantum yield is reduced significantly with increasing hydrogen-bond donating power of the medium, because hydrogen bonding that involves the electrons around the carbonyl oxygen atom will promote the nonradiative deactivation pathway by vibrational excitation of the resulting O–H group. However, coordination of a lanthanum(III) ion to the carbonyl oxygen atom cannot lead to deactivation through that mechanism. Instead, intersystem crossing to a triplet state promoted by the heavy metal ion could be a possible pathway for fluorescence quenching.

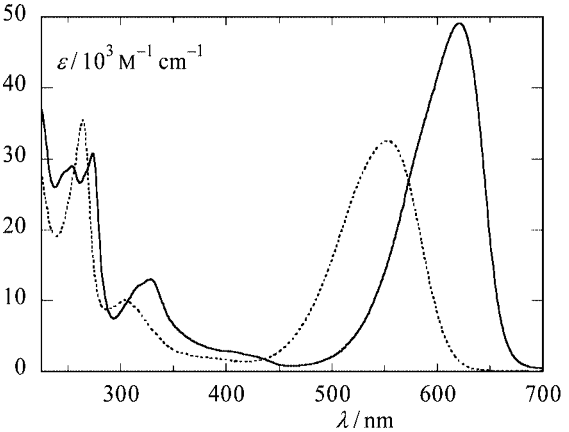

Figure 4. Optical absorption spectra of a 1.00×10^{-5} M MeCN solution of nr-C(O)OEt before (–) and after addition of a ten-fold excess of $La(CF_3SO_3)_3$ (---).

In summary, we have shown that the present derivatisation of nr ensures that complex formation with lanthanide(III) ions *does* take place in solution. An nr chromophore might thus serve as a VIS absorbing sensitizer for the NIR emitters Nd^{III}, Er^{III}, and Yb^{III}. Such systems might find use as luminescent tags in biological systems and have accordingly attracted interest in recent years.[14] Our investigations in this field are ongoing, and the results will be published in due time.

Experimental Section

Physical Methods and Materials: The starting material 6-carbethoxy-9-diethylamino-5*H*-benzo[*a*]phenoxazin-5-one [nr-C(O)-OEt] was prepared as described in the literature.[7] Infrared spectra were obtained with a FT-IR 1760X spectrometer. ^1H NMR studies were carried out with a Bruker 250 MHz instrument at room temperature with the δ values referenced to residual ^1H impurities in the solvent. Optical absorption spectra were recorded with a Cary 5E UV/Vis-NIR spectrophotometer. Fluorescence spectra were recorded on a Spex Fluorolog FL3-22. Elemental analyses (C, H, N) were performed at the Department of Chemistry, University of Copenhagen.

Single Crystals of Diaquabis(6-carbethoxy-9-diethylamino-5*H*-benzo[*a*]phenoxazin-5-one)tris(triflato-*O*)lanthanum(III) Monohydrate, $[La\{nr\text{-}C(O)OEt\}_2(OSO_2CF_3)_3(OH_2)_2]\cdot H_2O$ (1): A mixture of $La(CF_3SO_3)_3$ (50 mg, 0.085 mmol), nr-C(O)OEt (10 mg, 0.026 mmol), and CD_3CN (2 mL) was stirred, and undissolved $La(CF_3SO_3)_3$ was removed by centrifugation. The resulting blue solution was used for ^1H NMR spectroscopy. After several months at 298 K, green plate crystals of **1** separated out from this solution. The crystals were isolated by decantation and dried under a flow of nitrogen.

Tris(6-carbethoxy-9-diethylamino-5*H*-benzo[*a*]phenoxazin-5-one)lanthanum(III) Triflate Trihydrate, $[La\{nr\text{-}C(O)OEt\}_3](CF_3SO_3)_3\cdot 3H_2O$ (2): $La(CF_3SO_3)_3$ (200 mg, 0.34 mmol) was dissolved in dry acetonitrile (50 mL) with stirring. Then nr-C(O)OEt (50 mg, 0.13 mmol) was added, and the solution immediately turned dark blue. Slow evaporation of the solvent at room temperature over two weeks resulted in precipitation of a green microcrystalline material. The remaining mother liquor was decanted away, and the solid was washed thoroughly with water to remove excess $La(CF_3SO_3)_3$ and finally air-dried. Yield 40 mg (17%). $C_{72}H_{72}F_9LaN_6O_{24}S_3$ (1811.48): calcd. C 47.74, H 4.01, N 4.62; found C 47.81, H 3.69, N 4.63.

X-ray Crystallography: X-ray crystallographic study of **1**: $C_{49}H_{50}F_9LaN_4O_{20}S_3$, M = 1421.02, triclinic, $P\bar{1}$, a = 8.9240(9), b = 13.0080(12), c = 24.217(3) Å, α = 95.333(11), β = 93.696(9), γ = 90.493(9)°, V = 2793.2(5) Å^3, Z = 2, $\mu(\text{Mo-}K_\alpha)$ = 0.987 mm^{-1}, 83979 reflections measured with a Nonius KappaCCD area-detector system at 122(1) K in the θ range 1.57–27.99°, 13422 unique reflections [R(int) = 0.0588] were used in the data analysis. The structure was solved using SHELXS-97 and refined using SHELXL-97.[15] During the refinement of **1** disorder was observed that involved one of the ethyl groups in one of the nr ligands. The disorder was resolved by refining the ethyl group in two conformations. The refinement converged at R_1 = 0.0293 for 12035 observed reflections with $I > 2\sigma(I)$, wR_2 = 0.0671 for all unique reflections, S = 1.150, and an occupancy of 66% for the *cis* conformation of the disordered ethyl group. The anisotropic displacement parameters for all non-hydrogen atoms were refined. All hydrogen atoms were located in the difference Fourier map and included in the refinement riding on their parent atoms. The hydrogens on carbon were refined at idealised positions. Fourier peaks after the refinement were equal to 0.794 and –0.770 e/Å^3. CCDC-276918 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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[1] A. K. Dutta, K. Kamada, K. Ohta, *J. Photochem. Photobiol.* **1996**, *A93*, 57–64.
[2] J. F. Deye, T. A. Berger, A. G. Anderson, *Anal. Chem.* **1990**, *62*, 615–622.
[3] a) J. L. Meinershagen, T. Bein, *J. Am. Chem. Soc.* **1999**, *121*, 448–449; b) J. Hendriks, T. Gensch, L. Hviid, M. A. van der Horst, K. J. Hellingwerf, J. J. van Thor, *Biophys. J.* **2002**, *82*, 1632–1643; c) A. J. Carmichael, K. R. Seddon, *J. Phys. Org. Chem.* **2000**, *13*, 591–595; d) S. B. Ruvinov, X.-J. Yang, K. D. Parris, U. Banik, S. A. Ahmed, E. W. Miles, D. L. Sackett, *J. Biol. Chem.* **1995**, *270*, 6357–6369; e) D. L. Sackett, J. L. Knutson, J. Wolff, *J. Biol. Chem.* **1990**, *265*, 14899–14906; f) K. Goodlin, K. Johnson, L. Lefkowitz, B. W. Williams, *J. Chem. Educ.* **1994**, *71*, A8–A12.
[4] M. H. V. Werts, M. A. Duin, J. W. Hofstraat, J. W. Verhoeven, *Chem. Commun.* **1999**, 799–800.
[5] A. Døssing, *Eur. J. Inorg. Chem.* **2005**, 1425–1434 and references cited therein.
[6] a) L. C. D. Dias Jr., R. Custodio, F. B. T. Pessine, *Chem. Phys. Lett.* **1999**, *302*, 505–510; b) W.-G. Han, T. Liu, F. Himo, A. Toutchkine, D. Bashford, K. M. Hahn, L. Noodleman, *ChemPhysChem* **2003**, *4*, 1084–1094; c) C. M. Golini, B. W. Williams, J. B. Foresman, *J. Fluoresc.* **1998**, *8*, 395–404.
[7] J. Long, Y. M. Wang, T. Matsuura, J. B. Meng, *J. Heterocycl. Chem.* **1999**, *36*, 895–899.
[8] M. Colapietro, A. Domenicano, C. Marciante, G. Portaļone, *Acta Crystallogr. Sect. B* **1981**, *37*, 387–394.
[9] G. B. Jameson, B. M. Sheikh-Ali, R. G. Weiss, *Acta Crystallogr. Sect. B* **1994**, *50*, 703–707.
[10] H. J. Talberg, *Acta Chem. Scand.* **1977**, *A31*, 743–751.
[11] a) I. Aiello, M. Ghedini, M. La Deda, *J. Lumin.* **2002**, *96*, 249–259; b) M. La Deda, M. Ghedini, I. Aiello, T. Pugliese, F. Barigelletti, G. Accorsi, *J. Organomet. Chem.* **2005**, *690*, 857–861.
[12] V. Stužka, V. Šimánek, Z. Stránský, *Spectrochim. Acta A* **1967**, 2175–2183.
[13] A. Cser, K. Nagy, L. Biczók, *Chem. Phys. Lett.* **2002**, *360*, 473–478.
[14] S. Faulkner, J. L. Matthews, *Comprehensive Coordination Chemistry II* (Eds.: J. A. McCleverty, T. J. Meyer), vol. 9, Elsevier, Amsterdam, **2004**, 913–944.
[15] G. M. Sheldrick, *SHELXS-97* and *SHELXL-97*, University of Göttingen, Germany, **1997**.

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