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Charge transfer salts of the lanthanides: the crystal structure of $[Yb(Tp^{Me,Me})_2][TCNE]\cdot(THF)_6$

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Abstract

The reaction of $[Ln(Tp^{Me,Me})_2]$ (Ln = Sm, Eu, Yb) with TCNE and TCNQ gave good yields of the expected salt $[Ln(Tp^{Me,Me})_2]Y$ (Y = TCNE, TCNQ) as a THF solvate. The crystal structure of $[Yb(Tp^{Me,Me})_2][TCNE]\cdot(THF)_6$ was determined and shows the expected salt-like formulation, but shows no significant interionic contacts. The reactions with TCNQ produced less well-defined products with evidence for interionic contacts. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

The lanthanide elements have experienced a resurgence of interest in recent years as the strategies for controlling their labile coordination spheres have become more sophisticated. Although dominated by cyclopentadienyl ancillaries, which have proved useful in exploring both divalent and trivalent chemistry, a wide range of alternatives are being explored. These include organic ligands [1] and a wide range of nitrogen and oxygen donors, including chelating alkoxides [2,3], salen-type ligands [4], multidentate amides [5–7], porphyrinogens [8–11], and other macrocycles [12–14].

Pyrazolylborate ligands [15] have also featured prominently. Although initially used to bind to the trivalent metals [16], a number of groups have reported the isolation of divalent lanthanide compounds [17–21].

The initial hope of observing reactivity with $[Ln(Tp^{Me,Me})_2]$ comparable to that seen for the corresponding metallocenes was somewhat stymied by the observation that such complexes do not appear to form adducts with donor ligands such as CO, phosphines, pyridines, or isocyanides, nor do they react with simple olefins or alkynes [17,22]. This has been attributed, in large measure, to the steric protection afforded by the interlocked methyl groups on the ligands that prevent the close approach of the substrate. In contrast, for the less-encumbered Tp analogues, THF adducts of the type $[Ln(Tp)_2(THF)_2]$ are isolated [17,20]. Further reactivity studies with these complexes have not been reported.

On the other hand, it was possible to isolate tractable products for reactions of $[Ln(Tp^{Me,Me})_2]$ with more reducible substrates such as azobenzene [18], dioxygen [23], dichalcogenides [24–27], and several quinones [28,29]. In each case the reactivity appears driven by simple electron transfer. Thus, reactions with the more reducible TCNE and TCNQ were attempted with a view to preparing charge transfer salts.

2. Results

$[Ln(Tp^{Me,Me})_2]$ (Ln = Yb, Sm, Eu) was found to react readily with both TCNE and TCNQ to give highly coloured products (orange–brown and green respectively). Whereas the Yb reaction yielded mostly THF-soluble material, for Ln = Sm and Eu significant amounts of solid formed. After extraction of the solids with additional warm THF, appropriately coloured microcrystalline solids were obtained in moderate yields upon cooling the solutions. The resulting products were found to desolvate rapidly upon removal of the solvent. Elemental analysis of the soluble products indicated the formation of 1:1 products of the stoichiometry

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[Ln(Tp^{Me,Me})$_2$]TCNE (**1a** Ln = Yb; **2a** Ln = Sm; **3a** Ln = Eu) and [Ln(Tp^{Me,Me})$_2$]TCNQ (**1b** Ln = Yb; **2b** Ln = Sm; **3b** Ln = Eu). The products contained varying amounts of THF and reproducible elemental analyses were only obtained after drying the samples under dynamic vacuum for extended periods. All samples were NMR silent. The infrared spectra showed, in each case, a single peak assigned to a Tp^{Me,Me} ligand bound in tridentate fashion [30]. For the Yb complexes **1a** and **1b**, two sharp peaks associated with the TCNE or TCNQ anions were observed. The wavenumbers of these peaks were very similar to those observed previously for isolated TCNE or TCNQ anions (2148, 2187 cm^{-1} and 2152, 2181 cm^{-1} respectively) [31,32]. In order to verify the structure of these complexes, the crystal structure of **1a** was determined.

The crystal structure of **1a** consists of well-separated cations and anions together with six disordered molecules of THF per salt unit (Fig. 1). The Yb^{3+} cations are approximately octahedrally coordinated, with staggered Tp^{Me,Me} ligands, and have structural parameters that are very close to those observed by us previously for [Yb(Tp^{Me,Me})$_2$]OTf [33]. Thus the Yb–B separation and average Yb–N distances are 3.37 Å and 2.336(3) Å respectively compared with corresponding values of 3.35 Å and 2.318(5) Å in the triflate. These distances are also closely comparable to those observed in the corresponding samarium cations [Sm(Tp^{Me,Me})$_2$]-(TePh)$_3$ [24], [Sm(Tp^{Me,Me})$_2$]BPh$_4$ and [Sm(Tp^{Me,Me})$_2$]I [21], after correction for the contraction in ionic radius.

The bond distances in the TCNE molecule are very similar to those reported for other charge transfer complexes containing [TCNE]$^-$, such as [FeCp$_2^*$]TCNE [32]. Thus the anion is planar with average C≡N and C–CN distances of 1.133(7) Å and 1.427(7) Å respectively, and a C(16)–C(16A) distance of 1.398(11) Å. The corresponding bond lengths in the iron complex above are 1.140(4) Å, 1.417(2) Å and 1.392(9) Å respectively. A comparison of the structural features of the anion in **1** with those observed in neutral TCNE [34] shows that upon reduction the central C–C bond length increases by ca. 0.04 Å, the C≡N decreases slightly (by 0.03 Å) and the C–CN distance remains approximately unchanged. It is interesting to note that, despite the decrease in the C≡N bond length upon reduction from TCNE to [TCNE]$^-$, ν_{CN} also decreases (from 2228 and 2260 cm^{-1} in TCNE [35] to 2148 and 2187 cm^{-1} here). A similar result is obtained for other compounds containing polycyano anions, including [FeCp$_2^*$]TCNE [32], and may be related to the difficulty in determining short C–N distances accurately in X-ray structures [36]. A detailed experimental and theoretical analysis of the structural and spectroscopic properties (both vibrational and electronic) that accompany the one- and two-electron reductions of TCNE has been reported [37].

No significant interionic interactions are observed in the solid-state structure of **1a**. For example, the closest Yb···TCNE, Yb···Yb, and TCNE···TCNE contacts are 7.49 Å, 8.62 Å, and 10.64 Å respectively. A structure of this type is not expected to give rise to unusual magnetic or electronic properties for which close interactions are a prerequisite, such as those that have been reported for other charge transfer TCNE and TCNQ salts [38]. The uncertain stoichiometry of compounds **1**–**3** arising from the loss of solvent means that the study and interpretation of their magnetic properties are intrinsically complicated and were not attempted.

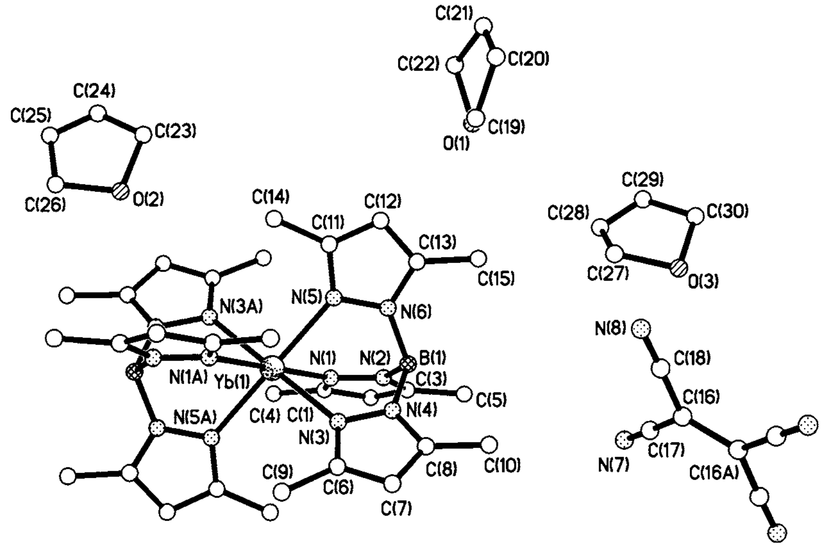

Fig. 1. The structure of [Yb(Tp^{Me,Me})$_2$][TCNE]·(THF)$_6$, **1a** (hydrogen atoms and THF minor disorder components omitted for clarity). Only three unique THF molecules are shown.

However, simple paramagnetic behaviour may be anticipated. It is pertinent to note that there has been a recent report of a transition-metal pyrazolylborate TCNQ complex, $[Fe(Tp^{Me,Me})_2]$TCNQ, in which there were no short-range interactions in the solid-state structure [39]. A study of the magnetic properties of this compound showed that, consistent with its structure, it behaved as a simple paramagnet. This arrangement of non-interacting cations and anions was attributed to the absence of available π-electron density on the $Tp^{Me,Me}$ ligand, in which respect it differs markedly from Cp*.

In contrast to the reasonably straightforward situation observed for the Yb complexes, the nature of the products obtained from the reactions of $[Ln(Tp^{Me,Me})_2]$ (Ln = Sm, Eu) is less clear. As mentioned above, in each case the reaction produced a mixture of THF-soluble and -insoluble materials. For TCNQ, both **2b** and **3b** failed to give reliable elemental analyses, presumably as a result of variable solvation by THF, and gave superimposable infrared spectra, suggesting very similar structures. However, both the CN stretching and the fingerprint regions differed significantly from that of the corresponding **1b**. In all cases the spectra were broader, but in addition the peaks were split. This may indicate some kind of interaction in the solid state or simply that more than one product had been formed. Furthermore, the insoluble material isolated from the TCNQ reactions darkened substantially (becoming dark green) when scraped from the walls of the Schlenk flask. We presume this to be due to a change in particle size rather than in structure. But it was not possible to confirm this, as we could not record spectra on undisturbed material. It is well established that both TCNE and TCNQ can coordinate to metal complexes in a variety of modes, and that this affects the number and positions of the C≡N stretching vibrations of the ligand [38]. Hence it is possible that the larger ions, Sm^{3+} and Eu^{3+}, allow the TCNQ anions to coordinate to the metal centre. We note, however, that this interaction must be fairly labile, since mass spectra recorded by fast atom bombardment only showed parent ion and fragmentation peaks associated with the fragment $[Ln(Tp^{Me,Me})_2]^+$.

In conclusion, we have prepared a pair of charge transfer salts of Yb. There is evidence for some possible cation–anion interactions in the corresponding Sm and Eu complexes, although no structural data are available to substantiate this. The difference may be attributed to the greater crowding of the metal centre for the smaller ytterbium ion. It may be possible to prevent counter-ion coordination by enforcing more complete steric saturation using the podand ligands such as Tp^{py} [40,41].

3. Experimental

All preparations and manipulations were carried out using standard Schlenk line and dry-box techniques in an atmosphere of dinitrogen [42,43]. Oxygen-free nitrogen was purified by passage over columns containing 3 Å molecular sieves and MnO [44]. All solvents were pre-dried over 5 Å molecular sieves or sodium wire and distilled under nitrogen from appropriate drying agents, K (tetrahydrofuran), CaH_2 (acetonitrile), before use.

$[Ln(Tp^{Me,Me})_2]$ (Ln = Sm, Yb) was prepared by reaction of samarium diiodide and two equivalents of sodium hydro-tris-(3,5-dimethylpyrazolyl)borate [45]. $[Ln(Tp^{Me,Me,4\text{-}Et})_2]$ was prepared analogously using potassium hydro-tris-(3,5-dimethyl-4-ethylpyrazolyl)-borate [21,22]. $[Eu(Tp^{Me,Me})_2]$ and $[Eu(Tp^{Me,Me,4\text{-}Et})_2]$ were prepared by Na–Hg reduction of the trivalent triflates [33].

Infrared spectra were recorded as KBr pellets on a Nicolet 205 FTIR spectrometer. Elemental analyses were determined by Mr Alan Stones of the UCL Analytical Services.

3.1. Preparation of $[Yb(Tp^{Me,Me})_2]$TCNE, **1a**

$[Yb(Tp^{Me,Me})_2]$ (0.196 g, 0.255 mmol) and TCNE (0.033 g, 0.257 mmol) were mixed in a Schlenk flask under nitrogen. THF (20 cm^3) was added with stirring. The fuchsia-coloured solid dissolved rapidly to give a yellow–orange solution and a small amount of orange precipitate. The solution was filtered and the volume of the solution reduced to 15 cm^3 under reduced pressure. After warming slightly, to redissolve a small amount of solid, the solution was cooled to −25°C to give yellow–orange crystals that desolvated rapidly on removal of solvent. Yield: 0.150 g (66%).

Anal. Found: C, 48.66; H, 5.21; N, 22.96. Calc. for $C_{40}H_{52}B_2N_{16}OYb$ $\{[Yb(Tp^{Me,Me})_2]TCNE\cdot(THF)\}$ C, 49.65; H, 5.42; N, 23.16%. IR (KBr/cm^{-1}): 2566 (BH), 2181, 2152 (C≡N). MS (FAB^+, nitrobenzyl alcohol): *m/z* 768 $[Yb(Tp^{Me,Me})_2]^+$; 566 $[Yb(Tp^{Me,Me})(dmpz)]^+$; 364 $[Yb(Tp^{Me,Me})]^+$; 269 $[Yb(dmpz)]^+$.

3.2. Preparation of $[Sm(Tp^{Me,Me})_2]$TCNE·THF, **2a**

$[Sm(Tp^{Me,Me})_2]$ (0.194 g, 0.260 mmol) and TCNE (0.033 g, 0.258 mmol) were mixed in a Schlenk flask under nitrogen. THF (20 cm^3) was added with stirring. The purple solid dissolved rapidly and an orange solution formed from which a red–brown solid slowly precipitated. The solution was filtered and the residue extracted with THF (2 × 20 cm^3). The volume of the solution was reduced to 30 cm^3 under reduced pressure and the solution cooled to −25°C to give a red–brown crystalline solid. Yield: 0.060 g (24%). Further concentration of the solution followed by cooling gave a second crop of material (0.015 g) that appeared to be slightly contaminated with a yellow material.

Anal. Found: C, 50.89; H, 5.56; N, 23.72. Calc. for $C_{40}H_{52}B_2N_{16}OSm$ {[Sm($Tp^{Me,Me}$)$_2$]TCNE·(THF)} C, 50.84; H, 5.55; N, 23.72%. IR (KBr/cm^{-1}): 2554 (BH), 2197, 2155 (C≡N). MS (FAB$^+$, nitrobenzyl alcohol): *m/z* 746 [Sm($Tp^{Me,Me}$)$_2$]$^+$; 544 [Sm($Tp^{Me,Me}$)(dmpz)]$^+$; 342 [Sm(dmpz)$_2$]$^+$.

3.3. Preparation of [Eu($Tp^{Me,Me}$)$_2$]TCNE, **3a**

[Eu($Tp^{Me,Me}$)$_2$] (0.150 g, 0.201 mmol) and TCNE (0.026 g, 0.203 mmol) were mixed in a Schlenk flask under nitrogen. THF (20 cm^3) was added with stirring. The orange material dissolved rapidly and an orange solution formed from which a red–brown solid slowly precipitated. The solution was filtered and the residue extracted with THF (2×10 cm^3). The volume of the solution was reduced to 20 cm^3 under reduced pressure and the solution cooled to −25°C to give a red–brown crystalline solid. Yield: 0.040 g (21%).

Anal. Found: C, 50.24; H, 5.30; N, 23.59. Calc. for $C_{40}H_{52}B_2EuN_{16}O$ {[Eu($Tp^{Me,Me}$)$_2$]TCNE·(THF)} C, 50.76; H, 5.54; N, 23.68%. IR (KBr/cm^{-1}): 2554 (BH), 2197, 2155 (C≡N). MS (FAB$^+$, nitrobenzyl alcohol): *m/z* 747 [Eu($Tp^{Me,Me}$)$_2$]$^+$; 545 [Eu($Tp^{Me,Me}$)(dmpz)]$^+$; 458 [Eu($Tp^{Me,Me}$)]$^+$; 248 [Eu(dmpz)]$^+$.

3.4. Preparation of [Yb($Tp^{Me,Me}$)$_2$]TCNQ, **1b**

[Yb($Tp^{Me,Me}$)$_2$] (0.211 g, 0.275 mmol) and TCNQ (0.056 g, 0.274 mmol) were mixed in a Schlenk flask under nitrogen. THF (40 cm^3) was added and the mixture stirred rapidly for 1 h. The fuchsia solid dissolved rapidly to give a deep-green solution and a dark-green solid. The solvent was removed under reduced pressure and the sticky residue extracted into acetonitrile. Cooling to −25°C gave a green microcrystalline product. Yield: 0.130 g (50%).

Anal. Found: C, 52.67; H, 4.99; N, 22.13. Calc. for $C_{44}H_{52}B_2N_{16}O_{0.5}Yb$ {[Yb($Tp^{Me,Me}$)$_2$]TCNQ·(0.5THF)} C, 52.45; H, 5.20; N, 22.24%. IR (KBr/cm^{-1}): 2566 (BH), 2181, 2152 (C≡N). MS (FAB$^+$, nitrobenzyl alcohol): *m/z* 768 [Yb($Tp^{Me,Me}$)$_2$]$^+$; 566 [Yb($Tp^{Me,Me}$)(dmpz)]$^+$; 364 [Yb(dmpz)$_2$]$^+$; 269 [Yb(dmpz)]$^+$. UV–Vis (THF/nm): 422, 749, 767, 850.

3.5. Preparation of [Sm($Tp^{Me,Me}$)$_2$]TCNQ, **2b**

[Sm($Tp^{Me,Me}$)$_2$] (0.181 g, 0.243 mmol) and TCNQ (0.050 g, 0.245 mmol) were mixed in a Schlenk flask under nitrogen. THF (40 cm^3) was added at −78°C and the mixture allowed to warm with stirring overnight to give a dark-green solution and a pale-green precipitate. After filtration the residue was dried under dynamic vacuum to give a pale-green solid (150 mg), which failed to dissolve in either THF or acetonitrile and darkened substantially on scraping from the walls with a spatula. Removal of THF from the filtrate yielded a small amount of a dark-green solid. Yield: 0.025 g (11%).

Soluble portion: IR (KBr/cm^{-1}): 2555 (BH), 2196, 2182, 2118 (C≡N). MS (FAB$^+$, nitrobenzyl alcohol): *m/z* 746 [Sm($Tp^{Me,Me}$)$_2$]$^+$; 544 [Sm($Tp^{Me,Me}$)(dmpz)]$^+$; 343 [Sm(dmpz)$_2$]$^+$.

Insoluble portion: IR (KBr/cm^{-1}): 2556 (BH), 2200, 2186, 2149, 2133 (C≡N). MS (FAB$^+$, nitrobenzyl alcohol): *m/z* 746 [Sm($Tp^{Me,Me}$)$_2$]$^+$; 544 [Sm($Tp^{Me,Me}$)(dmpz)]$^+$; 343 [Sm(dmpz)$_2$]$^+$.

3.6. Preparation of [Eu($Tp^{Me,Me}$)$_2$]TCNQ, **2c**:

The preparation of **2c** was analogous to that of **2b**.

Soluble portion: IR (KBr/cm^{-1}): 2555 (BH), 2199, 2183, 2119 (C≡N). MS (FAB$^+$, nitrobenzyl alcohol): *m/z* 747 [Eu($Tp^{Me,Me}$)$_2$]$^+$; 545 [Eu($Tp^{Me,Me}$)(dmpz)]$^+$; 458 [Eu($Tp^{Me,Me}$)]$^+$; 248 [Eu(dmpz)]$^+$.

Insoluble portion: IR (KBr/cm^{-1}): 2555 (BH), 2203, 2186, 2155, 2132 (C≡N). MS (FAB$^+$, nitrobenzyl alcohol): *m/z* 747 [Eu($Tp^{Me,Me}$)$_2$]$^+$; 545 [Eu($Tp^{Me,Me}$)(dmpz)]$^+$; 458 [Eu($Tp^{Me,Me}$)]$^+$; 248 [Eu(dmpz)]$^+$.

3.7. X-ray diffraction study of **1a**

Crystal data for **1a**: $[C_{30}H_{54}B_2N_{12}Yb]^+[C_6N_4]^-\cdot(OC_4H_8)_6$, orange crystal of dimensions $0.78 \times 0.42 \times 0.33$ mm^3, $M = 1328.16$, triclinic space group $P\bar{1}$ $a = 8.6167(5)$, $b = 14.1546(9)$, $c = 14.7438(9)$ Å, $\alpha = 72.247(2)$, $\beta = 79.609(2)$, $\gamma = 79.668(2)$°, $U = 1669.61(18)$ Å^3, $Z = 1$, $F(000) = 692$, $D_c = 1.321$ g cm^{-3}, μ(Mo–K$_\alpha$) = 1.460 mm^{-1}, $T = 180$ K. 9072 reflections (6334 unique with $R_{int} = 0.0203$) were collected on a Bruker AXS SMART 1K CCD area detector diffractometer with narrow frames (0.3° in ω) and three-dimensional profile fitting using graphite-monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.710\ 73$ Å). Data were corrected semi-empirically for absorption based on symmetry-equivalent and repeated reflections. Data were ca. 97% complete to $2\theta = 50°$, with $2\theta_{max} = 52.8°$. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 values. All non-H atoms were refined anisotropically, except those in the three crystallographically unique, twofold disordered, THF molecules, which were refined isotropically with restraints on geometry; H atoms were constrained. Final $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2} = 0.0823$ {where $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ and $P = (F_o^2 + 2F_c^2)/3$} for 379 refined parameters, conventional $R = 0.0308$ [for F values of 6334 data with $F^2 > 4\sigma(F^2)$]. The largest features in the final difference synthesis were within ± 0.92 e$^-$ Å^{-3}. Programs: Bruker AXS

SHELXTL [46] for structure solution and refinement and molecular graphics, Bruker AXS SMART (control), and SAINT (integration) and local programs [47].

4. Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 146696 for compound **1a**. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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