Inorg. Chem. **2005**, *44*, 584–593

Inorganic Chemistry
Article

Tris(dithiolene) Complexes of Neodymium and Cerium: Mononuclear Species, Chains, and Honeycomb Networks

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Received July 16, 2004

Reactions of $Ln(BH_4)_3(THF)_3$ (Ln = Nd, Ce) and M_2dddt (M = Na, K; dddt = 5,6-dihydro-1,4-dithiine-2,3-dithiolate) in THF or pyridine gave, after addition of 18c6 (18-crown-6), several crystalline compounds which all contain the tris(dithiolene) $Ln(dddt)_3$ unit. Crystals of $[Na(18c6)(py)_2]_2[Na(18c6)(py)][Nd(dddt)_3(py)]\cdot 3py$ (**1**·3py) are built up from discrete mononuclear cationic and anionic species whereas crystals of $\{[Na(18c6)(py)_2]_{0.5}[Na(18c6)(py)_{1.5}][Na_{1.5}Nd(dddt)_3]\}_\infty$ (**2**) are composed of discrete $[Na(18c6)(py)_x]^+$ cations and polymeric anionic two-dimensional layers in which the $Nd(dddt)_3$ units are linked to three neighbors by sodium atoms to form a honeycomb network. Analysis of the temperature dependence of the molar magnetic susceptibility of **2** shows that $\chi_M T$ decreases from 1.63 cm^3 K mol^{-1} at 300 K down to 0.6 cm^3 K mol^{-1} at 5 K, due to the crystal-field splitting of the $^4I_{9/2}$ free-ion state. Complexes $\{[Na_3(18c6)_{1.5}Nd(dddt)_3(THF)]\cdot 3THF\}_\infty$ (**3**·3THF) and $\{[K_3(18c6)_{1.5}Nd(dddt)_3(py)]\cdot 3py\}_\infty$ (**4**·3py) exhibit neutral polymeric layers with the $Nd(dddt)_3$ units linked by $M_2(18c6)$ fragments. In the cerium compound $\{[Na_2(18c6)Na(py)_2Ce(dddt)_3(py)]\cdot 3py\}_\infty$ (**5**·3py), each $Ce(dddt)_3$ unit is linked to two neighbors only by $Na_2(18c6)$ moieties, giving infinite zigzag chains.

Introduction

Much attention is paid to the diversity of dithiolene complexes of the main group and d transition metals which exhibit interesting structures and physicochemical properties and find applications as molecular precursors of conducting, magnetic, and optical materials.[1,2] In contrast, such complexes of the f-elements are quite uncommon, although they seem attractive in view of their coordination flexibility, redox behavior, and paramagnetism which could be the source of novel structures and electronic interactions. A very few entries into lanthanide and actinide dithiolene compounds have been opened. Tang et al. found that addition of K_2dmit (dmit = 2-thioxo-1,3-dithiole-4,5-dithiolate) to $LnCl_3$ in the presence of 1,10-phenanthroline (phen) gave the mono(dithiolene) complexes $K_2[LnCl_3(dmit)(phen)_2]\cdot 6H_2O$ (Ln = La, Nd, Sm, Gd, Er, Y) which behave as insulators and were transformed into typical semiconductors upon doping with iodine.[3] Baux et al. obtained a compound analyzed as Gd_2(tto) from the reaction of $GdCl_3$ and the tetraethylammonium salt of tetrathiooxalate (tto).[4] However, none of those complexes has been characterized by X-ray diffraction analysis. More recently, we reported that $[U(COT)(BH_4)_2]$ (COT = η-C_8H_8) reacted with Na_2dddt to afford the anionic complex $[U(COT)(dddt)_2]^{2-}$,[5] and with the dithiocarbonates dddtCO and dmioCO (dddtCO = 5,6-dihydro-1,3-dithiolo-[4,5-b][1,4]dithiine-2-one, dmioCO = 1,3,4,6-tetrathiapentalene-2,5-dione) to give the neutral compounds $[U(cot)(dithiolene)]_2$ and a series of Lewis base adducts of general formula $[U(COT)(dithiolene)(L)_n]$ [dithiolene = 5,6-dihydro-1,4-dithiine-2,3-dithiolate (dddt), 1,3-dithiole-2-one-4,5-dithiolate (dmio), or 1,3-dithiole-4,5-dithiolate (mdt)];[6] the X-ray crystal structures of these mono- and bis(dithiolene) orga-

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10.1021/ic049055i CCC: \$30.25

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Published on Web 01/13/2005

nouranium complexes revealed the interaction between the C=C double bond of the dithiolene ligand and the metal center. These investigations were facilitated by our experience of the monocyclooctatetraenyl uranium compounds which are in most cases easily identified by NMR spectroscopy and adopt the usual four-legged piano-stool configuration.[7] After these first studies, we decided to prepare homoleptic dithiolene compounds of the f-elements, expecting that their high coordination numbers and fluxional character, together with the bridging capacity of the sulfur atoms, would lead to the creation of unpredicted and more complicated structures which could be solved only with the help of crystallography. The syntheses were limited to two early members of the lanthanide series, cerium and neodymium, because the ionic radii of their trivalent ions are very similar to that of uranium(III),[8] permitting careful comparison of analogous 4f and 5f compounds;[9] the possibility to obtain a cerium(IV) derivative which could be compared with its uranium(IV) counterpart was also attractive. Reactions of $Ln(BH_4)_3(THF)_3$ (Ln = Ce, Nd) and UCl_4 with M_2dddt (M = Na, K) in the presence of 18c6 (18-crown-6) gave a variety of crystalline products, from mononuclear species to two-dimensional polymers, depending on the quantity of 18c6, the nature of the Ln and M metals, and the solvent. Here we report the syntheses and X-ray crystal structures of the tris(dithiolene) complexes of cerium(III) and neodymium(III), and in the following paper, we will present the tris and tetrakis(dithiolene) compounds of uranium(IV).[10]

Experimental Section

All reactions were carried out under argon (<5 ppm oxygen or water) using standard Schlenk-vessel and vacuum-line techniques or in a glovebox. Solvents were dried by standard methods and distilled immediately before use. The ^{1}H NMR spectra were recorded on a Bruker DPX 200 instrument and referenced internally using the residual protio solvent resonances relative to tetramethylsilane (δ 0). Elemental analyses were performed by Analytische Laboratorien at Lindlar (Germany). The crystalline compounds are sensitive to the thermal dissociation of lattice solvent, and so, the experimentally determined elemental analyses are often found to be lower than the computed analyses.

Syntheses. The precursors $Nd(BH_4)_3(THF)_3$,[11] Na_2dddt, and K_2dddt[12] were prepared by published methods; $Ce(BH_4)_3(THF)_3$ was synthesized in 72% yield from $CeCl_3$ using a procedure similar to that for the Nd analogue, but with a large excess of $NaBH_4$ (10 equiv) and by heating the reaction mixture under reflux for 35 days. ^{1}H NMR (THF-d_8, 23 °C): δ 31.6 (br, BH_4).

[$Na_3(THF)_{1.5}Nd(dddt)_3$]. A flask was charged with $Nd(BH_4)_3(THF)_3$ (231 mg, 0.57 mmol), and THF (50 mL) was condensed in. Addition of Na_2dddt (516 mg, 2.28 mmol) led to the immediate color change of the solution, from purple to green. After stirring for 3 days at 20 °C, a white precipitate of $NaBH_4$ was deposited. The solution was filtered and evaporated to dryness, leaving a green-yellow powder. The latter was then extracted in THF (40 mL), and some more $NaBH_4$ was eliminated by filtration. From the ^{1}H NMR spectra, the green powder of [$Na_3(THF)_{1.5}Nd(dddt)_3$] obtained after evaporation of the solvent was contaminated with 0.5 mol equiv of $NaBH_4$. Yield: 500 mg (99%). The difficulty in eliminating $NaBH_4$ from the powder does not permit us to rule out the formation of an "ate" complex in the solid state. ^{1}H NMR (pyridine-d_5, 23 °C): δ 3.53 (s, 12H, dddt), 3.66 (m, 6H, THF), 1.62 (m, 6H, THF), 1.41 (q, J = 80 Hz, 2H, $NaBH_4$). ^{1}H NMR (THF-d_8, 23 °C): δ 3.36 (s, 12H, dddt), −0.53 (q, J = 80 Hz, 2H, $NaBH_4$).

[$Na(18c6)(py)_2]_2[Na(18c6)(py)][Nd(dddt)_3(py)]\cdot 3py$ (1·3py) and $\{[Na(18c6)(py)_2]_{0.5}[Na(18c6)(py)_{1.5}][Na_{1.5}Nd(dddt)_3]\}_\infty$ (2). Pentane was carefully layered on a solution of [$Na_3(THF)_{1.5}Nd(dddt)_3$] (250 mg) and 18c6 (3−10 equiv) in pyridine (5 mL). After 5 days, orange crystals of **1**·3py and green crystals of **2** were deposited together. With 3 equiv of crown ether, compound **2** was largely predominant. Yield of hand separated crystals: 150 mg (39%). The crystals were dried under vacuum to give a green powder of general formula $Na_3Nd(dddt)_3(18c6)_{1.5}(py)_{2.5}$. Anal. Calcd for $C_{42.5}H_{60.5}N_{2.5}O_9S_{12}Na_3Nd$: C, 37.85; H, 4.52; N, 2.60. Found: C, 37.53; H, 4.68; N, 2.58. The relative proportion of **1** was increased with the amount of added crown ether, up to ca. 95% with 6 equiv of 18c6. Yield of hand separated crystals: 250 mg (46%). The orange crystals were dried under vacuum to give an orange powder of general formula $Na_3Nd(dddt)_3(18c6)_3(py)_{4.5}$. Anal. Calcd for $C_{70.5}H_{106.5}N_{4.5}O_{18}S_{12}Na_3Nd$: C, 44.49; H, 5.64; N, 3.31; S, 20.22. Found: C, 43.16; H, 5.57; N, 3.65; S, 19.00. ^{1}H NMR of **1**·3py (pyridine-d_5, −35 °C): δ 3.39 (s, 12H, dddt), 3.20 (s, 72H, 18c6). ^{1}H NMR of **2** (pyridine-d_5, 23 °C): δ 4.09 (s, 12H, dddt), 3.44 (s, 36H, 18c6).

$\{[Na_3(18c6)_{1.5}Nd(dddt)_3(THF)]\cdot 3THF\}_\infty$ (3·3THF). Pentane was carefully layered on a solution of [$Na_3(THF)_{1.5}Nd(dddt)_3$] (ca 6 mg) and 10 mol equiv of 18c6 (18 mg) in THF (0.5 mL). After 5−10 days, few green crystals of **3**·3THF were deposited together with a sticky off-white powder; crystals of suitable quality could not be obtained in sufficient quantity for chemical analyses.

$\{[K_3(18c6)_{1.5}Nd(dddt)_3(py)]\cdot 3py\}_\infty$ (4·3py). A flask was charged with $Nd(BH_4)_3(THF)_3$ (414 mg, 1.02 mmol), K_2dddt (820 mg, 3.17 mmol), and 18c6 (865 mg, 3.27 mmol), and pyridine (60 mL) was condensed in. After stirring for 3 days at 20 °C, the green precipitate was filtered off, washed with pyridine, and dried under vacuum. This powder was insoluble in pyridine unless more than 3 mol equiv of 18c6 was added, and the ^{1}H NMR spectrum showed the presence of KBH_4 (ca. 1.3 equiv). The borohydride was eliminated by successive extractions with pyridine in the presence of 18c6. Thus, the green powder (1200 mg) was stirred for 2 days in a solution of the crown ether (200 mg) in pyridine (30 mL), filtered off, and dried under vacuum; this operation was repeated twice for complete removal of KBH_4. The resulting green powder (808 mg, 53%) was dissolved in pyridine (60 mL) in the presence of 18c6 (400 mg). Slow diffusion of pentane into this solution led to the formation of green crystals of **4**·3py. Yield: 240 mg (36%). The crystals were dried under vacuum to give a green powder of general formula $K_3Nd(dddt)_3(18c6)_{1.5}(py)_{1.5}$. Anal. Calcd for $C_{37.5}H_{55.5}N_{1.5}O_9S_{12}K_3$-

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Nd: C, 34.18; H, 4.24; N, 1.60; S, 29.20. Found: C, 33.36; H, 4.66; N, 1.77; S, 28.90. The crystals are insoluble in pyridine, precluding NMR spectra to be recorded.

$\{[Na_2(18c6)Na(py)_2Ce(dddt)_3(py)]\cdot3py\}_\infty$ (5·3py). A flask was charged with $Ce(BH_4)_3(THF)_3$ (436 mg, 1.09 mmol), and THF (50 mL) was condensed in. The colorless solution immediately turned yellow upon addition of Na_2dddt (856 mg, 3.78 mmol). After stirring for 12 h at 20 °C, the solution was filtered, and addition of 18c6 (858 mg, 3.25 mmol) led to the precipitation of a yellow powder which was filtered off, washed with THF (100 mL), and dried under vacuum. The powder was contaminated with 0.5 equiv of $NaBH_4$. The difficulty in eliminating $NaBH_4$ from the powder does not permit us to rule out the formation of an "ate" complex in the solid state. Yield: 1265 mg (85%). Slow diffusion of pentane into a pyridine solution of this powder afforded yellow crystals of **5**·3py. Yield 250 mg (20%). The crystals were dried under vacuum to give a yellow powder of general formula $Na_3Ce(dddt)_3(18c6)(py)_2$. Anal. Calcd for $C_{34}H_{46}N_2O_6S_{12}Na_3Ce$: C, 34.82; H, 3.95; N, 2.39; S, 32.82. Found: C, 34.59; H, 4.11; N, 2.58; S, 33.07. ^1H NMR (pyridine-d_5, 23 °C): δ 3.21 (s, 12H, dddt), 3.32 (s, 24H, 18c6).

Crystallographic Data Collection and Structure Determination. The data were collected at 100(2) K on a Nonius Kappa-CCD area detector diffractometer[13] using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The crystals were introduced in glass capillaries with a protecting "Paratone-N" oil (Hampton Research) coating. The unit cell parameters were determined from 10 frames, then refined on all data. A 180° φ-range was scanned with 2° steps during data collection. The data were processed with *DENZO-SMN*.[14] The structures were solved by direct methods (**1**·3py and **2**) or by Patterson map interpretation (**3**·3THF−**5**·3py) with *SHELXS-97* and subsequent Fourier-difference synthesis and refined by full-matrix least-squares on F^2 with *SHELXL-97*.[15] Absorption effects were corrected empirically with the program *DELABS* from *PLATON*.[16] The correct enantiomorph in **1**·3py was determined from the value of the Flack parameter [−0.018(12)].[17] Despite different alkali metal ions and solvent molecules, compounds **3**·3THF and **4**·3py crystallize in the same space group, with very similar unit cell parameters.

Some disorder on counterions or solvent molecules is present, in greater or lesser extent, in all these structures. In compound **2**, one of the pyridine molecules bound to Na(4) [containing atom N(2)] is disordered over two positions related by the symmetry center, which are very close to each other, one of them bound to Na(4) and the other to Na(4′) [the latter related to Na(4) by the symmetry center]; since both positions cannot be occupied simultaneously, this pyridine molecule has been affected with a 0.5 occupancy parameter. Three pyridine molecules in **4**·3py and two in **5**·3py are disordered over two positions which were refined with occupancy parameters constrained to sum to unity. In compounds **1**·3py, **4**·3py, and **5**·3py, some pyridine solvent molecules were further refined as idealized hexagons. In **3**·3THF, the disorder affecting one crown ether and the three solvent THF molecules could only be partly solved; one carbon atom of the crown ether and two from a THF molecule were found to be disordered over two positions which have been attributed a 0.5 occupancy factor whereas all other atoms in these moieties had to be refined with restraints on bond lengths and displacement parameters. The highest residual electron density peak in this compound is located near a carbon atom of the badly resolved crown ether moiety. Some short H···H contacts involving the protons of badly behaving solvent or crown ether moieties in compounds **3**·3THF and **5**·3py are likely due to the imperfect description of the disordered nature of these molecules.

Compound **4**·3py was found to undergo a temperature-dependent phase transition: the triclinic phase present at 100 K is replaced by a trigonal phase at room temperature (293 K). In the latter, the Nd atom is located on the 3-fold axis, and the three dddt ligands and three potassium ions are symmetry-related. As a consequence, the pyridine bound to Nd is disordered over three positions at 60° from each other. No other important variation of the structure is observed. This phase transition is thus an order/disorder one, between a low-temperature low-symmetry phase and a high-temperature high-symmetry disordered one. Determination of the unit cell at different temperatures indicates that the transition occurs at approximately 260−270 K. Due to extended disorder, the room temperature structure could not be properly refined. Crystal data of the high-symmetry phase: $C_{50}H_{68}K_3N_4NdO_9S_{12}$, $M = 1515.34$, trigonal, space group $P\bar{3}$, $a = b = 19.4602(17)$ Å, $c = 10.3386(4)$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $V = 3390.7(4)$ Å^3, $Z = 2$, $D_c = 1.484$ g cm^{-3}, $\mu = 1.370$ mm^{-1}, $F(000) = 1554$.

All non-hydrogen atoms were refined with anisotropic displacement parameters (except the disordered ones in **2**) with some restraints on bond lengths and/or displacement parameters for some disordered or badly behaving atoms, as indicated above. Hydrogen atoms were introduced at calculated positions, except in disordered parts for compounds **2**−**5**·3py, and were treated as riding atoms with a displacement parameter equal to 1.2 times that of the parent atom. Crystal data and structure refinement details are given in Table 1. The molecular plots were drawn with *SHELXTL*[18] and *ORTEP-3/POV-Ray*.[19]

Magnetic Measurements. Temperature dependence of the molar magnetic susceptibility of **2** was determined on a 40 mg polycrystalline sample at 3000 G using a Quantum Design SQUID magnetometer MPMS-5 in the 5−300 K range. The data were corrected for the sample holder and for the diamagnetic contribution evaluated at 600×10^{-6} cm^3 mol^{-1}.

Results and Discussion

Syntheses. We first tried to prepare lanthanide dithiolene complexes by treating the chlorides $NdCl_3$ and $CeCl_3$ with the sodium salt of the dddt anion in THF, but no reaction was observed, even at 65 °C, certainly because of the insolubility of the reactants. We then used the borohydrides $M(BH_4)_3(THF)_3$ (M = Nd, Ce) which were shown to be valuable precursors of various organometallic derivatives.[11] Reaction of $Nd(BH_4)_3(THF)_3$ with a slight excess of Na_2dddt in THF gave, after filtration of the solution and evaporation to dryness, the tris(dithiolene) compound $[Na_3(THF)_{1.5}Nd(dddt)_3]$ which was isolated as a green powder in almost quantitative yield but was contaminated with ca. 0.5 mol equiv of $NaBH_4$. The ^1H NMR spectra in THF-d_8 or pyridine-d_5 show a singlet at δ 3.36 or 3.53, respectively, attributed to magnetically equivalent dddt

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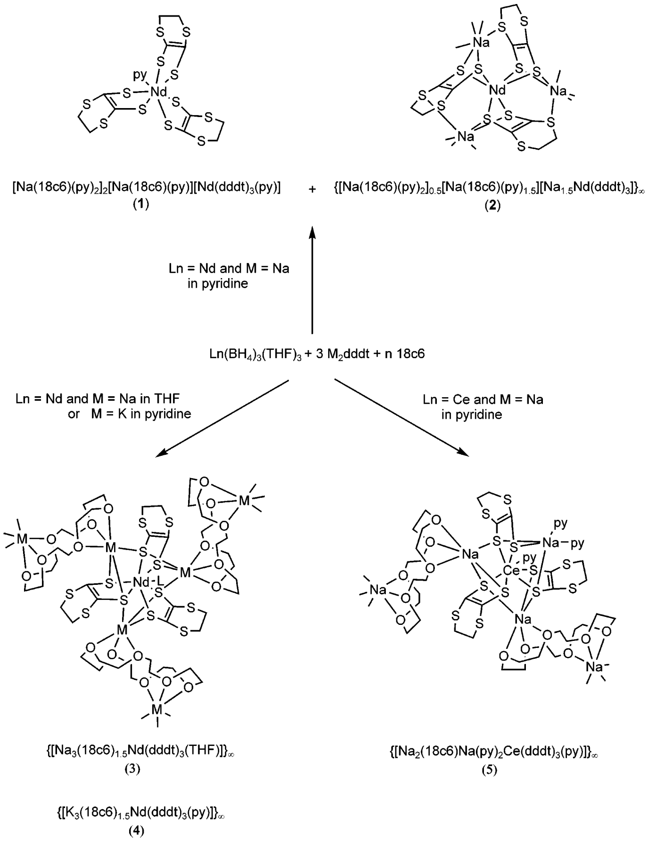
Table 1. Crystal Data and Structure Refinement Details for Complexes **1**−**5**

	1·3py	**2**	**3**·3THF	**4**·3py	**5**·3py
empirical formula	$C_{93}H_{129}N_9Na_3NdO_{18}S_{12}$	$C_{42.5}H_{60.5}N_{2.5}Na_3NdO_9S_{12}$	$C_{46}H_{80}Na_3NdO_{13}S_{12}$	$C_{50}H_{68}K_3N_4NdO_9S_{12}$	$C_{54}H_{66}CeN_6Na_3O_6S_{12}$
M/g mol^{-1}	2258.98	1348.36	1439.03	1515.34	1488.94
cryst syst	monoclinic	triclinic	triclinic	triclinic	triclinic
space group	$P2_1$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	13.8785(13)	14.2753(9)	10.1439(8)	10.3168(5)	12.1362(11)
b/Å	24.3573(13)	14.8237(7)	18.4818(11)	18.6713(14)	16.705(2)
c/Å	16.9363(17)	17.0518(10)	19.2305(15)	19.3117(15)	17.7897(16)
α/deg	90	114.415(3)	118.159(4)	118.759(3)	74.203(6)
β/deg	110.288(4)	91.860(3)	92.238(4)	90.469(4)	74.938(7)
γ/deg	90	116.398(3)	94.281(4)	92.869(4)	73.106(6)
V/Å^3	5370.0(8)	2837.8(3)	3158.4(4)	3254.8(4)	3256.0(6)
Z	2	2	2	2	2
D_{calc}/g cm^{-3}	1.397	1.578	1.513	1.546	1.519
μ(Mo Kα)/mm^{-1}	0.795	1.431	1.294	1.427	1.155
F(000)	2358	1380	1490	1554	1526
reflns collected	36715	19776	21654	22537	22290
indep reflns	19752	9993	10947	11415	11412
obsd reflns [$I > 2\sigma(I)$]	12156	7138	7873	8587	7527
R_{int}	0.107	0.066	0.078	0.059	0.076
params refined	1221	634	703	758	779
R1	0.069	0.059	0.074	0.044	0.061
wR2	0.170	0.146	0.194	0.107	0.153
S	0.975	1.035	1.063	1.033	1.015
$\Delta\rho_{min}$/e Å^{-3}	−1.01	−0.72	−1.28	−0.61	−0.95
$\Delta\rho_{max}$/e Å^{-3}	0.76	1.22	1.53	0.60	1.10

ligands, in addition to the signals of THF and $NaBH_4$. No crystals were deposited from pyridine or THF solutions of the green powder which presumably contain mixtures of soluble “ate” complexes in which the alkali metal ions are scrambling over the dithiolene sulfur atoms; for inducing crystallization of more rigid compounds, variable amounts of 18c6, from 3 to 10 mol equiv with respect to neodymium, were added to these solutions. Three products were thus obtained, containing the $Nd(dddt)_3$ moiety in distinct forms which are represented in Scheme 1. Slow diffusion of pentane into the pyridine solutions led to the formation of orange and green crystals together; the relative proportion of the orange crystals was found to increase with the amount of added crown ether (ca 95% with 6 equiv of 18c6). X-ray diffraction analysis revealed that the orange crystals of the pyridine solvate $[Na(18c6)(py)_2]_2[Na(18c6)(py)][Nd(dddt)_3(py)]\cdot 3py$ (**1**·3py) are composed of discrete mononuclear cationic and anionic species, whereas the green crystals of $\{[Na(18c6)(py)_2]_{0.5}[Na(18c6)(py)_{1.5}][Na_{1.5}Nd(dddt)_3]\}_\infty$ (**2**) are built up from discrete $[Na(18c6)(py)_x]^+$ cations and infinite anionic 2D layers in which the $Nd(dddt)_3$ units are linked to three neighbors by Na atoms in an hexagonal network.

Only green crystals were deposited in small quantity from solutions of $[Na_3(THF)_{1.5}Nd(dddt)_3]$ in THF, after addition of 10 mol equiv of 18c6. Their structure is quite distinct from that of **2** since it exhibits neutral polymeric layers of composition $\{[Na_3(18c6)_{1.5}Nd(dddt)_3(THF)]\}_\infty$ (**3**); the major difference between the crystal structures of **2** and **3**·3THF is that the latter does not contain separated cationic sodium species, the $Nd(dddt)_3$ moieties being linked by $Na_2(18c6)$ fragments in place of single Na atoms.

Scheme 1. Synthesis of the Tris(dithiolene) Lanthanide Complexes and Representation of the Environment of the $Ln(dddt)_3$ Units



The potassium salt of the dddt anion did not react with $Nd(BH_4)_3(THF)_3$ in THF, even in the presence of 18c6; this lack of reactivity can be attributed to the insolubility of K_2dddt. The same mixture in pyridine gave a green powder which was soluble in this solvent only after addition of more than 3 mol equiv of crown ether. Green crystals of $\{[K_3(18c6)_{1.5}Nd(dddt)_3(py)]\cdot 3py\}_\infty$ (**4**·3py) were formed upon slow diffusion of pentane into this pyridine solution, whatever the quantity of added 18c6, between 3 and 10 mol equiv. The structure of **4**·3py is remarkably quite identical to that of **3**·3THF, the THF molecules having been replaced with pyridine molecules and the Na atoms with K atoms.

Treatment of Ce(BH$_4$)$_3$(THF)$_3$ with Na$_2$dddt in THF afforded, after addition of 3−10 mol equiv of 18c6, a yellow-green powder which was recrystallized in a mixture of pyridine and pentane to give yellow crystals of composition {[Na$_2$(18c6)Na(py)$_2$Ce(dddt)$_3$(py)]·3py}$_\infty$ (**5**·3py); these consist of infinite zigzag chains in which the Ce(dddt)$_3$ units are linked to two neighbors by Na$_2$(18c6) fragments.

The variety of structures for complexes **1**−**5** isolated from reactions of Ln(BH$_4$)$_3$(THF)$_3$ (Ln = Ce, Nd) and M$_2$dddt (M = Na, K) in pyridine or THF in the presence of 18c6, which all contain the Ln(dddt)$_3$ moiety, results from the diverse and competitive modes of complexation of the alkali metal ions with the sulfur atoms of the dddt ligands, the oxygen atoms of the crown ether, and the nitrogen atoms of the pyridine solvent. It is only in pyridine that the sodium ions were inserted into the crown ether to give separated [Na(18c6)(py)$_x$]$^+$ ions in **1** and **2**; the relative proportions of these complexes, that is the number of [Na(18c6)(py)$_x$]$^+$ ions which are formed, are easily explained by the quantity of added crown ether. That the solvent plays an important role in the synthesis of these compounds is illustrated by the formation of **3**·3THF instead of **2** when pyridine was replaced with THF; in that case, dissociation into cationic and anionic species did not occur. One could imagine that **2** would be in equilibrium with {[Na$_3$(18c6)$_{1.5}$Nd(dddt)$_3$(py)]}$_\infty$, the analogous complex of **3** in pyridine (or the sodium analogue of **4**), following reversible insertion of [Na(18c6)]$^+$ into Na−S bonds of the anionic layer. However, this insertion was not evidenced by increasing the concentration of the solution from 0.01 to 0.15 M, since only the green crystals of **2** were invariably formed and the analogous complex of **3** was not obtained in pyridine. The nature of the alkali and lanthanide metals has also a great influence on the structure of the products, as shown by the synthesis of **4** or **5** instead of **2** when K$_2$dddt or Ce(BH$_4$)$_3$(THF)$_3$ was used in place of Na$_2$dddt or Nd(BH$_4$)$_3$(THF)$_3$, respectively. The different factors which may contribute to the unpredicted building of compounds **1**−**5**, in particular the coordinating ability of the solvent and the ligands, the ionic radii of the metals, and the solubility of the products, are difficult to rationalize; nevertheless, the serendipitous syntheses of the complexes were reproducible.

Crystal Structures. Views of the separated anion [Nd(dddt)$_3$(py)]$^{3-}$ in **1**·3py, the anionic fragment [Na$_{1.5}$Nd(dddt)$_3$]$^{1.5-}$ in **2**, and the neutral units [Na$_3$(18c6)$_3$Nd(dddt)$_3$(THF)] in **3**·3THF and [Na$_2$(18c6)$_2$Na(py)$_2$Ce(dddt)$_3$(py)] in **5**·3py are shown in Figures 1−4, respectively; the structure of **4**·3py resembles that of **3**·3THF, as outlined in Scheme 1. Selected bond distances and angles are listed in Table 2.

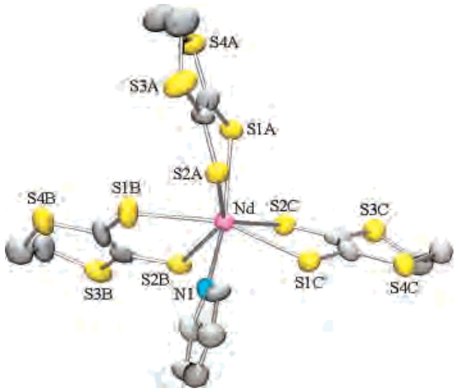


Figure 1. View of the [Nd(dddt)$_3$(py)]$^{3-}$ anion in **1**·3py. The hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

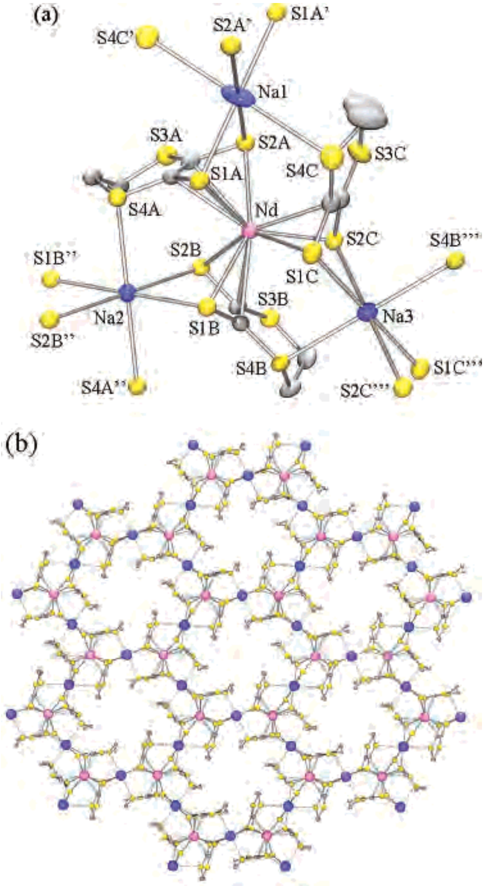


Figure 2. (a) View of the anionic fragment [Na$_{1.5}$Nd(dddt)$_3$]$^{1.5-}$ in **2**. The hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: ′ = −*x*, −*y*, 1 − *z*; ″ = 1 − *x*, −*y*, 1 − *z*; ‴ = 1 − *x*, 1 − *y*, 1 − *z*. (b) View of the honeycomb arrangement in compound **2**. Counterions have been omitted.

In all the complexes, except **2**, an extra THF or pyridine molecule is coordinated to the Ln(dddt)$_3$ fragment. As often observed in compounds of general formula [M(bidentate ligand)$_3$(unidentate ligand)], the polyhedron chosen to describe best the metal environment in **1** is somewhat arbitrary;[20] one can see the Nd atom in a very distorted square-capped trigonal prismatic configuration, the trigonal faces of the prism being defined either by the S(1A), S(2A), S(1B) and S(1C), S(2B), S(2C) atoms or S(1A), S(1C), S(2C) and S(1B), S(2B), N(1) atoms with N(1) or S(2A) in capping positions. Such a geometry was found in the β-diketonate complexes [Yb(MeCOCHCOMe)$_3$(H$_2$O)][21] and [Lu(Bu-

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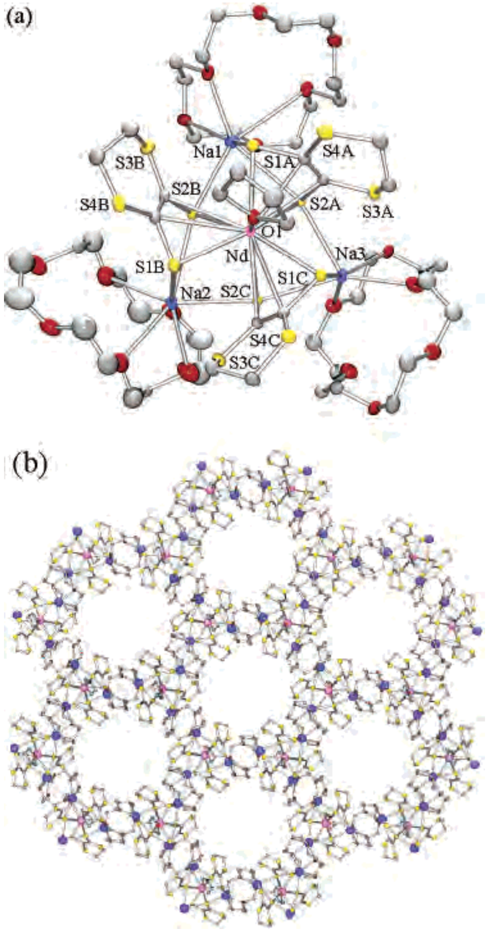

Figure 3. (a) View of the neutral unit $[Na_3(18c6)_{1.5}Nd(dddt)_3(THF)]$ in **3**·3THF. The hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level. (b) View of the honeycomb arrangement in compound **3**. Only one component of the disordered part of one crown ether is represented. Solvent molecules have been omitted.

$COCHCOBu)_3(NC_5H_4Me)]$.[22] In contrast, the six sulfur atoms and the nitrogen or oxygen atom in complexes **3** and **4** clearly define a capped octahedron with O(1) or N(1) in the unique capping position, the Nd−O(1) or Nd−N(1) line being a pseudo-3-fold axis of symmetry (Figure 5); this stereochemistry is the only one which renders the three bidentate ligands equivalent.[20] The two triangles S(1A)−S(1B)−S(1C) and S(2A)−S(2B)−S(2C) are nearly equilateral, in almost perfectly staggered conformation, and their dihedral angle is equal to 0.22(2)° and 2.29(1)° in **3** and **4**, respectively. The Nd atom which lies inside the S_6 octahedron is closer to the $S(1)_3$ than to the $S(2)_3$ plane, at distances of 0.5747(18) and 1.9220(17) Å in **3**, and 0.6454(7) and 1.9244(7) Å in **4**. The cerium atom in **5** exhibits the same capped octahedral coordination geometry, but slightly more distorted, the dihedral angle between the $S(1)_3$ and $S(2)_3$ triangles being equal to 6.92(6)°. This stereochemistry is also that adopted by the β-diketonate complexes $[Y(PhCOCHCOMe)_3(H_2O)]$[23] and $[Ho(PhCOCHCOPh)_3(H_2O)]$.[24]

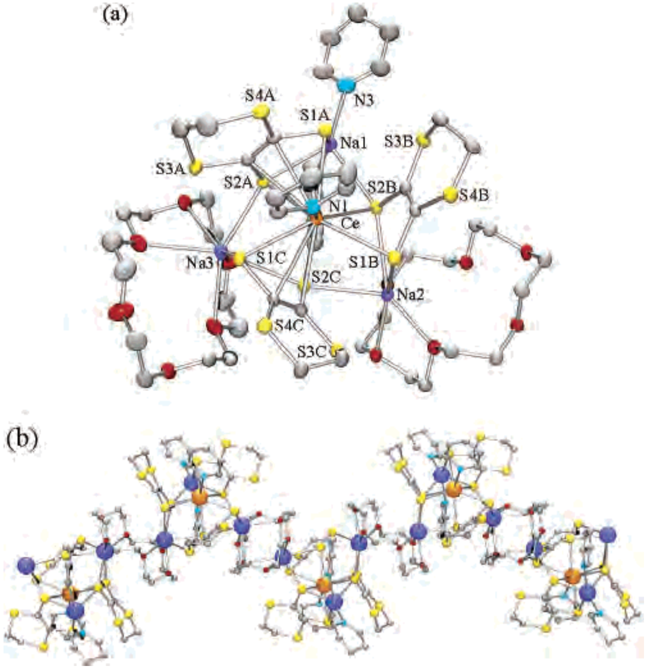

Figure 4. (a) View of the neutral unit $[Na_2(18c6)Na(py)_2Ce(dddt)_3(py)]$ in **5**·3py. The hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level. (b) View of the zigzag chain arrangement in compound **5**. Only one component of the disordered pyridine molecule [containing N(3)] is represented. Solvent molecules have been omitted.

Complex **2** is the sole true homoleptic tris(dithiolene) lanthanide compound, and it is interesting to compare its structure with those of the d transition metal analogues. The latter have attracted much attention because they were found to adopt in many cases a near trigonal prismatic coordination geometry while the majority of all six-coordinate complexes exhibit an octahedral geometry.[25−27] These distortions away from the octahedron toward the trigonal prism have been explained by interligand bonding interactions within the S_3 triangles and by optimum overlap between the sulfur π orbitals and the metal d orbitals.[26] The structure of **2** does not depart from this trend since the six S atoms are at the vertices of a distorted trigonal prism around the metal center (Figure 6). The two nearly equilateral triangles S(1A)−S(1B)−S(1C) and S(2A)−S(2B)−S(2C) are almost parallel, with a dihedral angle of 1.87(6)°, and are twisted from their eclipsed conformation by an angle of ca. 20°. The neodymium atom is located between these planes at a distance of 1.7515(11) and 1.4867(11) Å, respectively. The coordination geometry of **2** is similar to that found in the tris(dithiophosphinate) complexes $[Ln(S_2PCy_2)_3]$ (Ln = Pr, Sm, Dy, Lu)[28] but is different from that of the homoleptic thiolate com-

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Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes **1**−**5**

	1·3py	**2**	**3**·3THF	**4**·3py	**5**·3py
Ln−S(1A)	2.817(2)	2.8292(18)	2.874(2)	2.8780(12)	2.922(2)
Ln−S(2A)	2.861(2)	2.8819(19)	2.906(2)	2.8989(12)	2.8944(17)
Ln−S(1B)	2.872(3)	2.8469(19)	2.871(2)	2.8435(12)	2.9303(18)
Ln−S(2B)	2.869(2)	2.8748(18)	2.899(2)	2.9109(12)	2.9567(18)
Ln−S(1C)	2.870(3)	2.8347(19)	2.881(2)	2.9053(13)	2.9168(18)
Ln−S(2C)	2.853(3)	2.8710(19)	2.883(2)	2.9421(12)	2.9136(19)
Ln−N(1) or Nd−O(1)	2.658(7)		2.553(6)	2.695(4)	2.717(6)
Ln−C(1A)		2.928(7)	3.051(9)	3.088(4)	3.037(7)
Ln−C(2A)		2.946(7)	3.082(8)	3.087(4)	3.041(7)
Ln−C(1B)		2.897(7)	3.243(9)	2.996(5)	3.260(7)
Ln−C(2B)		2.910(7)	3.208(9)	3.013(5)	3.221(7)
Ln−C(1C)		2.881(7)	3.090(8)	3.338(5)	3.102(7)
Ln−C(2C)		2.933(7)	3.101(8)	3.325(5)	3.083(7)
M(1)−S(1A)		2.7968(19)	2.892(4)	3.1293(15)	2.934(3)
M(1)−S(2A)		2.8629(18)	3.168(4)	3.2830(16)	2.762(3)
M(2)−S(1B)		2.8469(18)	2.966(4)	3.2407(15)	3.025(3)
M(2)−S(2B)		2.9480(19)	3.153(4)	3.3011(16)	2.995(3)
M(3)−S(1C)		2.9126(19)	2.919(4)	3.2318(15)	2.927(3)
M(3)−S(2C)		2.9439(19)	3.063(4)	3.2463(16)	3.071(3)
Na(1)−S(4C)		3.446(2)			
Na(2)−S(4A)		3.0675(19)			
Na(3)−S(4B)		3.090(2)			
M(1)−S(2B)			2.915(4)	3.2386(16)	2.786(3)
M(2)−S(2C)			2.958(4)	3.2023(16)	2.878(3)
M(3)−S(2A)			2.958(4)	3.1504(16)	2.829(4)
S(1A)−Ln−S(2A)	72.23(7)	71.43(5)	70.34(6)	69.41(3)	68.95(5)
S(1B)−Ln−S(2B)	71.64(10)	71.47(5)	70.51(6)	70.93(3)	68.45(5)
S(1C)−Ln−S(2C)	71.30(7)	71.75(5)	69.98(6)	69.73(3)	69.28(5)
θ_{A}[a]	22.77(12)	85.06(4)	78.95(7)	77.85(3)	82.34(5)
θ_{B}	8.35(14)	87.81(5)	69.08(7)	80.74(4)	72.73(6)
θ_{C}	13.53(12)	87.33(6)	77.57(6)	65.84(4)	79.22(5)

[a] θ_{A}, θ_{B}, and θ_{C} are the folding angles of the dddt ligands A, B, and C, respectively.

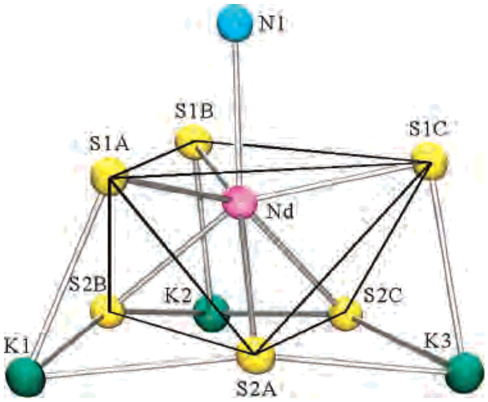

Figure 5. Metal environment in **4**·3py. Displacement ellipsoids are drawn at the 50% probability level. The distorted octahedron is shown as black lines.

pounds $[Li(tmeda)]_3[Ln(S^tBu)_6]$ (Ln = Sm, Yb) which adopt an octahedral configuration.[29]

The average Nd−S distance in **1**, 2.86(2) Å, is only slightly shorter than that of 2.886(13) or 2.90(3) Å in **3** and **4**, respectively; this difference is smaller than that expected for terminal and bridging SR groups, ca. 0.2 Å, and can be accounted for by the more important electron density on the metal center of **1**. The average Nd−S distance is also equal to 2.86(2) Å in **2** and reflects, with respect to **3** and **4**, the lower coordination number of the complex. The mean metal−sulfur bond length of 2.92(2) Å in **5** is 0.02−0.03 Å longer than in **3** and **4**, in agreement with the variation in the ionic radii of the trivalent Nd and Ce ions.[8] These bond lengths can be compared with those of 2.93(1) Å in $[Nd(C_5H_4Me)_2(\mu\text{-}SPh)(THF)]_2$,[30] 2.91(3) Å in $[Na(THF)_2\{Nd(C_8H_8)\}_2(\mu\text{-}S^tBu)_3]$,[11] 2.88(1) Å in $[Ce(C_5H_4{}^tBu)_2(\mu\text{-}S^iPr)]_2$,[31] and 3.02(2) Å for the bridging thiolate ligands in $[Ce(SC_6F_5)_2(\mu\text{-}SC_6F_5)(THF)_3]_2$.[32] In line with the increase of the M−S bond lengths from **1** to **5**, the chelate bite angles S−Ln−S slightly decrease with average values of 71.7(4)° in **1**, 71.6(1)° in **2**, 70.3(2)° in **3**, 70.0(7)° in **4**, and 68.9(3)° in **5**.

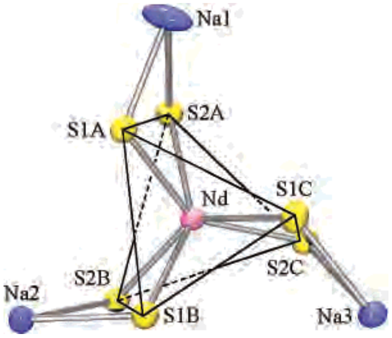

Figure 6. Metal environment in **2**. Displacement ellipsoids are drawn at the 50% probability level. The distorted trigonal prism is shown as black lines.

The S_4C_2 fragment of the dddt ligands is planar with an rms deviation of 0.01−0.07 Å and forms a dihedral angle θ with the corresponding S−Ln−S plane. The average value of θ in **2**, 86.7(12)°, is ca. 10° larger than in **3**−**5**, likely reflecting the lower coordination number of the metal which facilitates the folding of the ligand. However, the folding θ angles in **1** are much smaller than in **3**−**5**; this difference can be explained by the greater electron density on the metal which weakens the interaction between an empty metal orbital and the HOMO of the dithiolene ligand.[12,33] The large folding of the dddt ligands in compounds **2**−**5** brings the C(1) and C(2) atoms in close contact with the metal center, at an average distance of 2.92(2), 3.13(7), 3.14(14), and 3.12(9) Å, respectively. These values can be compared with the mean metal−carbon bond lengths in the neodymium arene complexes $[Nd(C_6H_6)(AlCl_4)_3]$ [2.93(2) Å][34] and $[Nd(OC_6H_3\text{-}Ph_2\text{-}2,6)_3]$ [3.04(8) Å],[35] and with the contacts of 2.83(3)−3.23(4) Å between the neodymium and the *ortho* and *meta* carbon atoms of two phenyl rings of the tetraphenylborate anion in $[Nd(C_5Me_5)_2][BPh_4]$.[36] In all the complexes **1**−**5**, the characteristics of the dithiolene ligands, i.e., the average

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C(sp^2)−S and C=C distances of 1.76(3)−1.774(6) Å and 1.355(7)−1.37(2) Å are consistent with those found in [Mo(C_5H_5)$_2$(dddt)] [1.76(1) and 1.33(1) Å][37] and [Na(18c6)(THF)][U(C_8H_8)(dddt)$_2$] [1.75(1) and 1.36(1) Å],[5] indicating that the dithiolate ligand is effectively in its dianionic form.

With the exception of **1**, the Ln(dddt)$_3$ units are surrounded by three sodium or potassium atoms which form a nearly equilateral triangle, almost parallel to the S(1)$_3$ and S(2)$_3$ triangles, with a pseudo-3-fold axis containing the metal atom. In **2**, the Na$_3$ plane defines dihedral angles of 3.66(4)° and 1.80(5)° with the S(1)$_3$ and S(2)$_3$ planes, respectively. The Na$_3$ triangle is twisted with respect to the S(1)$_3$ and S(2)$_3$ triangles by an angle of ca. 30 and 9°, respectively (Figure 6), and is located between these S$_3$ planes at a distance of 0.6577(4) Å from the Nd atom, on the side of the S(1) atoms. The M$_3$ and S(1)$_3$ triangles in **3**−**5** are slightly rotated from their eclipsed conformation, by a twist angle of 10−20°, and the M$_3$ triangle is farther away than the staggered S(2)$_3$ triangle from the metal center, at a distance of 2.201(3), 2.3334(6), and 2.3979(16) Å, respectively (Figure 5). In all the complexes, each Na or K atom is bound to the S(1) and S(2) atoms of one dddt ligand and to one sulfur atom of another one, S(4) in **2** and S(2) in **3**−**5**; the S(2B) atoms are thus in triply bridging position in **3**−**5**. These differences between **2** and **3**−**5** are obviously related to the distinct coordination of the alkali metal atoms. The Na atoms in **2** are lying on inversion centers and bridge the Nd(dddt)$_3$ units whereas the Na or K atoms in **3**−**5** are bound, in addition to the three sulfur atoms of the Ln(dddt)$_3$ unit, to three or four oxygen atoms of a bridging 18c6 molecule or, in the case of Na(1) in **5**, to two nitrogen atoms of pyridine ligands; the middle of the Na···Na segment in each Na$_2$(18c6) moiety is an inversion center. The six-coordinate Na atoms in **2**, **3**, and **5** are in distorted octahedral environment and the seven-coordinate ones in **3** [Na(2)] and **5** [Na(3)] in distorted capped octahedral environments; the Na(1) atom in **5** adopts a trigonal bipyramidal configuration with N(2) and S(1A) in apical positions. The geometry of the Na$_2$(18c6) moieties in **3** and **5** is very similar to that of Na$_2$(dicyclohexyl-18c6) which ensures the bridging of two Co(salen) units in [{Co(salen)Na}$_2$(dicyclohexyl-18c6)];[38] the Na−O distances are ranging between 2.417(11) and 2.856(6) Å with an average value of 2.5(2) Å which is identical to that found in the cobalt compound. The Na−S bond lengths in **2**, **3**, and **5** vary from 2.762(3) to 3.168(4) Å, except Na(1)−S(4C) in **2** which is equal to 3.446(2) Å; the average values of 2.99(18) Å in **2**, 3.00(10) in **3**, and 2.91(10) Å in **5** are quite similar to the Na−S distance in [Na(THF)$_3$]$_2$[U(SR)$_6$], 2.965(8) and 3.060(3) Å for R = ^{t}Bu or Ph respectively,[39] or the average Na−S distance of 2.9(1) Å for the NaS$_6$ octahedra of Na_3AsS_3.[40] The Na(1)−N(2) and Na(1)−N(3) bond lengths in **5**, 2.552(7) and 2.404(6) Å, are unexceptional; they are, for example, similar to those of 2.46(1) and 2.50(1) Å in [Sm(SePh)(py)$_2$(μ-SePh)$_3$Na(py)$_2$]$_2$,[41] and 2.56(2) Å in the [Na(py)$_6$]$^+$ cation.[42] The average Na−O, Na−S, and Na−N distances in **5** [2.53(10), 2.91(10), and 2.48(7) Å] can be compared with the corresponding values in the crown-ether-coordinated sodium pyridine-2-thiolate complexes [Na(15c5)(NC_5H_4S-2)] [2.5(1), 3.038(1), and 2.429(3) Å] and [Na(18c6)(NC_5H_4S-2)] [2.6(1), 2.764(1), and 2.649(2) Å].[43] The coordination mode of the K$_2$(18c6) unit in **4**, which is identical to that of Na$_2$(18c6) in **3**, is similar to that of K$_2$(dicyclohexyl-18c6) in [{K(OPh)$_2$}$_2$(dicyclohexyl-18c6)],[44] while the structure of the latter is very different from that of its sodium counterpart in which one sodium atom is coordinated to the six hexaether oxygen atoms and the other sodium atom is linked to only one of the crown oxygen atoms. The average K−O and K−S distances of 2.83(8) and 3.22(5) Å in **4** are normally larger than the mean Na−O and Na−S bond lengths in **3** and **5** and are similar to those of 2.90(2) and 3.2558(1) Å in [K(18c6)(NC_5H_4S-2)];[43] the mean K−O bond length can be compared with that of 2.84(8) Å in the aforementioned potassium phenoxide complex.[44] Distances of ca. 3.3−3.4 Å are observed between each potassium atom and the S(3) atom of the neighboring dddt ligand, likely reflecting weaker interactions; thus, there is some uncertainty in the K coordination number (six or seven). The crystal structures of the [Na(18c6)(py)$_x$]$^+$ cations (x = 1 or 2), present in **1** and **2**, have not been reported previously; the octahedral or hexagonal pyramidal coordination geometry of the alkali metal is identical to that found in [Na(18c6)(THF)$_2$]$^+$,[45] [K(18c6)(py)$_2$]$^+$,[46] or [Na(18c6)(OR$_2$)]$^+$ (R = Et or ^{i}Pr).[47] The Na−O and Na−N bond lengths, with average values of 2.72(12) and 2.47(5) Å, are unexceptional.

As indicated above, the anionic fragments [Na$_{1.5}$Nd(dddt)$_3$]$^{1.5-}$ in compound **2** are associated in a bidimensional coordination polymer with a honeycomb net structure represented in Figure 2b. Each roughly planar hexagonal cell consists of six Nd and six Na atoms held alternately in a ring by 18 dddt ligands. The Nd atoms constitute the trigonal nodes whereas the Na atoms act as spacers and define the sides of the hexagons, which have a length of 8.7169(9) Å. Each dddt ligand is bound to one Nd and two Na atoms and pertains to all three adjacent hexagonal cells around the Nd atom. These planar assemblages are parallel to the *ab* plane, and the successive layers, separated by ca. 15 Å, would define channels along the *c* axis, but for the presence of the [Na(18c6)(py)$_x$]$^+$ cations in the interlayer spaces. The mean

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planes defined by the six oxygen atoms of the two crystallographically independent crown ethers make dihedral angles of 71.64(8)° and 72.07(8)° with the honeycomb plane. When viewed along the *c* axis, the $[Na(18c6)(py)_2]^+$ cation projects alongside a hexagon side, with the Na atom superposed to that defining the side, whereas the disordered $[Na(18c6)(py)_{1.5}]^+$ moiety projects at the center of the hexagonal cell.

Honeycomb networks are also found in compounds **3** and **4** (Figure 3b), but the situation is quite different since these polymers are now neutral. The hexagonal cells comprise six Nd atoms as trigonal nodes and 12 M (Na in **3**, K in **4**) atoms, each side corresponding to a $M_2(18c6)$ fragment. The resulting size of the cells is larger than in **2**, with a side length of 11.9183(16) Å. In contrast to the planar hexagons found in **2**, the hexagonal rings in **3** and **4** are strongly puckered, with the Nd atoms alternately above and below the mean plane defined by the Na or K atoms. As in compound **2**, each dddt ligand is bound to one Nd and two M atoms. The 2D polymer formed is parallel to the *bc* plane, and hexagonal channels are formed along the *a* axis, with an effective inner diameter of ca. 8−9 Å (van der Waals radii excluded). The interlayer separation is close to the *a* parameter, 10.1439(8) and 10.3168(5) Å in **3** and **4**, respectively. In the absence of counterions, the channels are occupied by the solvent molecules only (much disordered in compound **4**).

Although honeycomb net structures are less frequent in metal−organic than in organic compounds,[48] several examples have been reported, with either ligand[49] or metal[50] moieties as trigonal nodes. In the case of rare earth metal ions, honeycomb networks have been considered in the search for new magnetic properties.[51]

In compound **5**, the arrangement around each lanthanide atom is nearly the same as in **3** and **4**, but one of the three sodium atoms is bound to two pyridine molecules instead of a crown ether. This results in an interruption of the bidimensional pattern and the formation of a zigzag polymeric chain running along the (101) direction, with successive cerium atoms separated by 11.5891(13) and 11.9471(14) Å and Ce···Ce···Ce angles of 105.610(10)° (Figure 4). Successive chains in the *bc* plane are offset with respect to the position they would occupy in a honeycomb arrangement, and as a result, no wide channel is formed.

Magnetic Properties. The peculiar honeycomb structure of the single true homoleptic complex **2** led us to further characterize its magnetic properties in the solid state.[52,53] The free-ion ground state of Nd(III) is $^4I_{9/2}$. The first excited state, $^4I_{11/2}$, is located at 2000 cm^{-1} above, so that it is fully depopulated, even at room temperature.[54] The Zeeman factor g_J is then equal to $^8/_{11}$, affording a $\chi_M T$ value of 1.64 cm^3 K mol^{-1}. The experimental $\chi_M T$ versus T curve for **2** is shown in Figure 7. At room temperature, $\chi_M T$ amounts to 1.65 cm^3 K mol^{-1} as predicted above from the free-ion $^4I_{9/2}$ ground state. Upon lowering the temperature, $\chi_M T$ decreases down to 0.6 cm^3 K mol^{-1}, indicating strong deviations from the Curie law. This behavior, already observed in molecular Nd complexes with (O, N) ligands, has been rationalized by Andruh et al.[52] from a contribution of the crystal field which splits the $^4I_{9/2}$ free-ion ground state into five Kramers doublets, equally populated at 300 K (hence the free-ion approximation value) but progressively depopulated as T decreases.

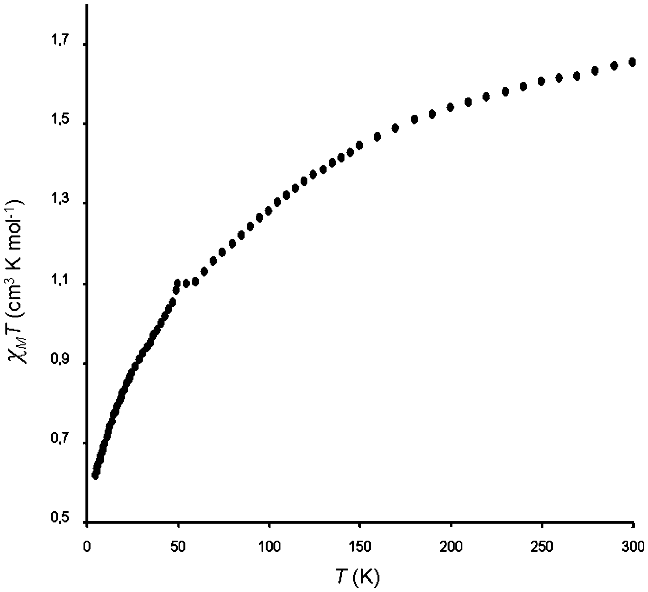

Figure 7. $\chi_M T$ versus T plot for **2**.

Conclusion

We have synthesized the first tris(dithiolene) complexes of an f element, which are also the first lanthanide dithiolene compounds to have been crystallographically characterized. The structure of these compounds, which all contain the $[Ln(dddt)_3]$ unit, is dependent on the nature of the lanthanide metal (Nd, Ce), the counterion (Na^+ or K^+), the solvent (THF or pyridine), and the amount of 18c6 which is necessary to induce crystallization. After the d transition metal complexes $[NEt_4]_3[Ru(mnt)_3]$,[55] $[PPh_4]_3[Cr(mnt)_3]$ (mnt = 1,2-dicyanoethylene dithiolate),[56] and $[PPh_4]_3[Co(dithiocrotonate)_3]$,[57] the compounds reported here are new trianionic tris(dithiolene) derivatives characterized by their crystal structure. The use of alkali metal ions in place of $[NEt_4]^+$ and $[PPh_4]^+$ allowed us to obtain, in addition to monomeric species, infinite chains in which each $Ln(dddt)_3$ unit is linked to two neighbors by $Na_2(18c6)$ fragments, or two-dimensional neutral or anionic

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layers in which each Ln(dddt)$_3$ unit is surrounded by three Na$_2$(18c6) fragments or Na atoms to form a honeycomb network.

Acknowledgment. We warmly thank Pr. M. Andruh, from the University of Bucarest (Romania), for enlightening discussions on the magnetic properties of those rare-earth complexes.

Supporting Information Available: Tables of crystal data, atomic positions and displacement parameters, anisotropic displacement parameters, bond lengths, and bond angles in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC049055I