Structure and Spectra of a Series of Eight-co-ordinate Complexes of Lanthanoids(III) with Diethyldithiocarbamate of General Formula Na[Ln(Et_2NCS_2)$_4$] (Ln = La to Yb, except Pm)

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A series of diethyldithiocarbamates (Et_2dtc) of all the lanthanoids from La to Yb, except Pm, of general formula $Na[Ln(Et_2dtc)_4]$ have been prepared. The *X*-ray crystal and molecular structure of the lanthanum complex has been determined from diffractometer data. Crystals are monoclinic, space group $P2_1$, with a = 21.154(13), b = 21.445(15), c = 15.584(9) Å, β = 101.56(4)°, Z = 8. The structure was refined by least-squares techniques to R 0.089 for 4 412 observed reflections. The structure consists of Na^+ and $[La(Et_2dtc)_4]^-$ ions; in the anion the lanthanum atom is co-ordinated by eight sulphur atoms forming a distorted dodecahedron. Conductance and spectral measurements show that the eight-co-ordinate structure persists in methyl cyanide solutions. The electronic spectra have been investigated for methyl cyanide solutions in the spectral range 5—39 kK, and bands attributed to electronic transitions of intraligand, charge-transfer, and *f–f* type. With the cerium(III) complex, intense bands at *ca.* 23 kK are attributed to *f–d* or inverted electron transitions.

DURING renewed interest in lanthanoid(III) compounds with donors other than oxygen and nitrogen, Brown *et al.* reported the isolation of two series of *NN*-diethyldithiocarbamates (Et_2dtc^-) of general formula $[Ln(Et_2dtc)_3]$ and $[NEt_4][Ln(Et_2dtc)_4]$.[1]

X-Ray powder diffraction results indicated that the $[NEt_4][Ln(Et_2dtc)_4]$ compounds are isostructural with $[NEt_4][Np(Et_2dtc)_4]$. The complete structure determination of the latter compound showed that the neptunium atom is co-ordinated by eight sulphur atoms arranged as a grossly distorted dodecahedron.[1] No electronic spectral data were reported but later Siddall and Stewart described the preparation and spectral properties of some di-isobutyldithiocarbamates of formula $[NHEt_3][Ln(Bu^i{}_2dtc)_4]$, where Ln = La, Pr, Nd, Sm, and Eu.[2] A few spectral measurements for unstable ethanolic solutions, of diethyldithiocarbamates of some lanthanoids, of uncertain composition, had been carried out by Jørgensen.[3]

In order to obtain detailed knowledge of the electronic spectral properties of the LnS_8 chromophores, we have prepared *NN*-diethyldithiocarbamates of all the lanthanoid(III) ions from La to Yb (except Pm). The compounds have general formulae $Na[Ln(Et_2dtc)_4]$ and this paper reports their preparation, conductivity, electronic and vibrational spectra, and the complete *X*-ray structural determination of $Na[La(Et_2dtc)_4]$.

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[1] D. Brown and D. G. Holah, *Chem. Comm.*, 1968, 1545; D. Brown, D. G. Holah, and C. E. F. Rickard, *ibid.*, 1969, 280; *J. Chem. Soc.* (*A*), 1970, 786.

[2] T. H. Siddall and W. E. Stewart, *J. Inorg. Nuclear Chem.*, 1970, **32**, 1147.

[3] C. K. Jørgensen, *Mol. Phys.*, 1962, **5**, 271.

TABLE 1

Analytical and physical data for $Na[Ln(Et_2dtc)_4]$

Compound	Colour	Analysis (%) * C	H	N	Λ/ S cm^2 mol^{-1} †
$Na[La(Et_2dtc)_4]$	White	31.8 (31.82)	5.6 (5.34)	7.5 (7.42)	93.5
$Na[Ce(Et_2dtc)_4]$	Bright yellow	32.0 (31.76)	5.5 (5.33)	7.4 (7.41)	
$Na[Pr(Et_2dtc)_4]$	Pale green	32.0 (31.73)	5.4 (5.33)	7.5 (7.40)	
$Na[Nd(Et_2dtc)_4]$	Pale lilac	31.4 (31.59)	5.4 (5.30)	7.2 (7.37)	
$Na[Sm(Et_2dtc)_4]$	Pale yellow	31.2 (31.34)	5.4 (5.26)	7.4 (7.31)	
$Na[Eu(Et_2dtc)_4]$	Brick-red	30.9 (31.28)	5.4 (5.25)	7.3 (7.29)	100.5
$Na[Gd(Et_2dtc)_4]$	White	30.7 (31.06)	5.2 (5.21)	7.3 (7.24)	
$Na[Tb(Et_2dtc)_4]$	White	31.2 (30.99)	5.2 (5.20)	7.3 (7.23)	
$Na[Dy(Et_2dtc)_4]$	White	30.7 (30.85)	5.2 (5.18)	7.0 (7.20)	
$Na[Ho(Et_2dtc)_4]$	Yellow-pink	30.8 (30.76)	5.3 (5.16)	7.2 (7.17)	92.0
$Na[Er(Et_2dtc)_4]$	Pink	30.9 (30.66)	5.0 (5.15)	7.0 (7.15)	
$Na[Tm(Et_2dtc)_4]$	White	30.7 (30.60)	5.1 (5.14)	7.3 (7.14)	
$Na[Yb(Et_2dtc)_4]$	Bright yellow	30.4 (30.44)	5.3 (5.11)	7.1 (7.10)	91.5

* Calc. values in parentheses. † For *ca.* 5×10^{-3} mol dm^{-3} solutions in methyl cyanide at 25 °C. Under the same conditions reference values are: 112 S cm^2 mol^{-1} for $Na[B(C_6H_5)_4]$ and 42 S cm^2 mol^{-1} for $Na(Et_2dtc)$.

EXPERIMENTAL

Preparation of the Compounds.—The anhydrous metal trichloride (5 mmol) in absolute ethanol (20 ml) was added to a solution of anhydrous sodium diethyldithiocarbamate (25 mmol) in ethanol (20 ml). After a few minutes, solvent was removed *in vacuo*, the residue extracted into anhydrous methyl cyanide (30 ml), and the filtered solution concentrated *in vacuo* to *ca.* 15 ml. By slow addition of anhydrous diethyl ether (200 ml) crystals of $Na[Ln(Et_2dtc)_4]$ separated, which were washed with ether and dried *in vacuo*. With the cerium(III) compound all operations were performed under pure nitrogen and with deoxygenated solvents. The bright yellow $Na[Ce(Et_2dtc)_4]$ darkens immediately in the presence of traces of oxygen. Table 1 reports analytical data, colours, and molar conductances of the compounds.

Spectral Measurements.—Solution spectra (5—40 kK) * were recorded with a Cary 17 spectrophotometer. Reflectance spectra were recorded with a Beckman DK 2 spectrophotometer equipped with a standard reflectance attachment and magnesium oxide as the reference.

Crystal Data.—$Na[La(Et_2dtc)_4]$, $C_{20}H_{40}LaN_4NaS_8$, $M = 754.98$, Monoclinic, $a = 21.154(13)$, $b = 21.445(15)$, $c = 15.584(9)$ Å, $\beta = 101.56(4)°$, $U = 6\,926.23$ Å^3, $D_c = 1.448$, $Z = 8$. $\lambda(Cu\text{-}K_\alpha) = 1.541\,8$ Å; $\mu(Cu\text{-}K_\alpha) = 143.79$ cm^{-1}. Space group $P2_1$.

Data Collection.—Intensity data were collected on a Philips automatic diffractometer with the ω—2θ scan technique. The K_α radiation was monochromatized by means of a flat graphite crystal. 4 635 reflections were measured within 2θ 10—100°, and of these 4 412 having $I > 2.5\sigma(I)$ were used for the structure determination. The standard deviation of an intensity was estimated according to the expression: $\sigma(I) = [P + 0.25(B_1 + B_2)(T_p/T_b)^2 + (kI)^2]^{\frac{1}{2}}$, where P is the peak count, B_1 and B_2 are the background counts, and T_p and T_b are the count times on the peak and background respectively. The constant k was estimated to be 1.27×10^{-2} by a least-squares analysis of the intensities of three standard reflections measured at regular intervals. Intensities were corrected for Lorentz-polarization and absorption effects.

Structure Determination and Refinement.—The solution of the structural problem appeared rather complicated, owing to the presence of four molecules in the asymmetric unit. Direct methods, however, with the use of the computer program MULTAN [4] readily gave the positions of the four independent lanthanum atoms and of most of the sulphur atoms. A series of successive electron-density syntheses showed most of the remaining atom positions. Great difficulties were encountered in the location of the carbon atoms of ethyl groups.

With 136 independent atoms for a total of 565 parameters the least-squares refinement was performed in blocks. A series of several cycles with anisotropic temperature factors for the lanthanum atoms and isotropic ones for the other atoms reduced the R factor, calculated over the independent observed reflections, to 0.089. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with weights from counting statistics. Atomic scattering factors were taken from ref. 5, that of lanthanum being corrected for the real and imaginary part of anomalous dispersion effects.[6] Final atomic parameters with their standard deviations are reported in Table 2. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21913 (24 pp., 1 microfiche).†

The 'X-ray '72' system of programs was used for all calculations.[7]

RESULTS AND DISCUSSION

Description of the Structure.—The structure of $Na[La(Et_2dtc)_4]$ consists of discrete $[La(Et_2dtc)_4]^-$ (Figure 1) and Na^+ ions. In the anions the lanthanum atoms are co-ordinated by eight sulphur atoms. The co-ordination polyhedron can be described as a distorted dodecahedron, very similar to that of neptunium in $[NEt_4][Np(dtc)_4]$.[1] An alternative description can be made in terms of an almost planar pentagonal arrangement of the sulphur atoms with one atom above and two below the plane. The four CS_2 groups are arranged at the vertices of a distorted tetrahedron with four angles of *ca.* 100° and two of *ca.* 135°.

The four independent polyhedra in the asymmetric unit are almost identical, slight differences in bond

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* 1 kK = 10^3 cm^{-1}.

† See Notice to Authors No. 7 in *J.C.S. Dalton*, 1976, Index issue.

[4] P. Main, M. M. Woolfson, and G. Germain, 'MULTAN, A Computer Programme for the Automatic Solution of Crystal Structures,' Centre Européen de Calcul Atomique et Moleculaire, Orsay, France, 1971.

[5] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[6] 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

[7] 'X-Ray '72,' Technical Report TR 192, 1972, University of Maryland, U.S.A., eds. J. M. Stewart, F. A. Kundell, and J. C. Baldwin.

TABLE 2

Positional parameters ($\times 10^4$), thermal parameters * (Å^2 $\times$ 10^3) with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	U_{11} *	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
La(1)	5 424(1)	7 828	921(2)	70(2)	95(3)	53(2)	6(2)	17(2)	−4(2)
La(2)	578(1)	9 459(2)	4 970(2)	73(2)	99(3)	73(3)	−3(2)	16(2)	−5(2)
La(3)	4 366(1)	2 487(2)	4 026(2)	69(2)	79(2)	53(2)	−7(2)	13(2)	0(2)
La(4)	495(1)	9 191(2)	−69(2)	83(2)	90(2)	68(2)	1(2)	7(2)	2(2)

Atom	x/a	y/b	z/c	U	Atom	x/a	y/b	z/c	U
S(1)	5 549(6)	8 596(6)	2 546(9)	82(4)	S(17)	3 492(5)	2 657(6)	2 305(8)	79(4)
S(2)	4 293(7)	8 383(7)	1 386(10)	106(5)	S(18)	3 816(6)	1 419(6)	3 034(9)	87(4)
S(3)	6 438(6)	7 038(6)	2 033(9)	81(4)	S(19)	5 438(6)	2 109(6)	3 155(9)	87(4)
S(4)	5 070(6)	6 710(6)	1 884(9)	86(5)	S(20)	5 226(6)	3 455(6)	3 403(9)	84(4)
S(5)	6 674(6)	8 386(7)	751(10)	105(5)	S(21)	3 779(6)	3 709(7)	4 421(10)	102(5)
S(6)	5 451(6)	8 812(6)	−430(9)	81(4)	S(22)	3 341(6)	2 507(6)	5 073(8)	74(4)
S(7)	5 597(6)	6 847(6)	−376(9)	89(5)	S(23)	4 739(6)	1 409(6)	5 206(9)	84(4)
S(8)	4 298(6)	7 419(6)	−492(9)	93(5)	S(24)	5 403(5)	2 628(6)	5 699(8)	76(4)
S(9)	2(6)	8 809(7)	3 345(9)	92(5)	S(25)	308(7)	8 096(8)	952(11)	127(6)
S(10)	−785(6)	9 715(7)	4 148(10)	97(5)	S(26)	1 482(7)	8 869(7)	1 506(11)	123(6)
S(11)	811(7)	10 539(7)	3 841(10)	99(5)	S(27)	866(8)	10 454(8)	489(11)	132(6)
S(12)	1 771(6)	9 521(7)	4 218(9)	100(5)	S(28)	−284(6)	9 917(7)	998(10)	99(5)
S(13)	1 423(7)	10 034(7)	6 528(10)	105(5)	S(29)	1 032(7)	8 261(7)	−1 164(10)	94(5)
S(14)	89(7)	10 444(7)	6 011(10)	113(5)	S(30)	1 654(6)	9 504(7)	−812(9)	90(4)
S(15)	34(7)	8 596(7)	6 043(10)	111(5)	S(31)	−229(7)	9 835(7)	−1 654(10)	109(5)
S(16)	1 298(7)	8 348(7)	5 711(11)	115(6)	S(32)	−764(7)	8 706(7)	−983(11)	114(6)
Na(1)	4 722(8)	2 807(9)	1 671(12)	90(6)	Na(3)	5 669(8)	7 397(9)	3 399(12)	93(7)
Na(2)	715(10)	9 285(11)	7 474(15)	132(8)	Na(4)	762(9)	9 635(10)	2 461(13)	110(7)
N(1)	4 516(22)	9 069(22)	2 885(32)	166(20)	N(9)	2 981(24)	1 660(24)	1 518(33)	150(22)
N(2)	5 920(21)	5 841(22)	1 856(31)	155(19)	N(10)	6 435(18)	2 898(20)	3 787(27)	144(16)
N(3)	6 624(20)	9 145(21)	−667(30)	151(19)	N(11)	2 933(17)	3 624(18)	5 405(25)	100(13)
N(4)	4 534(18)	6 216(18)	−868(26)	120(15)	N(12)	5 904(16)	1 487(17)	6 152(24)	102(13)
N(5)	−1 204(14)	9 156(14)	2 600(20)	65(10)	N(13)	1 279(32)	7 816(34)	2 489(46)	306(35)
N(6)	2 098(18)	10 725(18)	4 218(26)	121(15)	N(14)	−158(19)	11 080(19)	565(28)	124(16)
N(7)	911(19)	11 134(19)	6 834(28)	137(16)	N(15)	2 334(19)	8 418(19)	−614(27)	136(16)
N(8)	815(28)	7 358(30)	6 257(42)	187(31)	N(16)	−1 278(18)	9 250(19)	−2 469(27)	120(15)
C(1)	4 761(24)	8 771(27)	2 345(36)	110(22)	C(41)	3 456(19)	1 889(19)	2 315(28)	75(15)
C(2)	3 278(36)	8 960(37)	2 982(54)	220(39)	C(42)	3 074(37)	820(37)	1 259(51)	226(36)
C(3)	4 848(26)	9 187(28)	3 854(39)	143(21)	C(43)	2 818(33)	1 949(32)	714(45)	167(29)
C(4)	3 631(28)	9 323(29)	2 475(41)	194(26)	C(44)	2 612(40)	768(39)	1 648(57)	266(42)
C(5)	4 730(36)	9 794(38)	3 801(52)	203(36)	C(45)	2 349(38)	2 163(38)	965(54)	209(38)
C(6)	5 861(21)	6 500(22)	1 966(31)	101(17)	C(46)	5 723(17)	2 781(20)	3 405(27)	70(14)
C(7)	5 431(22)	5 350(23)	1 825(34)	106(18)	C(47)	6 732(31)	3 617(33)	4 360(49)	141(29)
C(8)	6 755(22)	5 651(23)	2 023(34)	93(18)	C(48)	6 839(25)	2 389(26)	3 649(38)	131(21)
C(9)	5 471(25)	5 146(26)	2 812(39)	161(22)	C(49)	6 955(40)	3 753(41)	3 542(60)	231(41)
C(10)	6 762(29)	5 503(31)	1 067(47)	153(28)	C(50)	6 924(31)	2 003(30)	4 455(44)	155(28)
C(11)	6 336(25)	8 845(26)	−74(37)	136(22)	C(51)	3 300(20)	3 256(20)	5 013(30)	87(16)
C(12)	6 275(26)	9 675(27)	−1 387(40)	155(22)	C(52)	2 782(21)	4 311(22)	5 254(32)	104(17)
C(13)	7 426(38)	8 988(38)	−456(55)	265(37)	C(53)	2 525(28)	3 318(29)	6 106(42)	172(26)
C(14)	6 350(29)	9 310(31)	−2 134(45)	174(27)	C(54)	3 143(25)	4 587(27)	5 975(36)	139(22)
C(15)	7 691(46)	9 361(48)	−309(69)	222(53)	C(55)	1 863(29)	3 153(29)	5 584(42)	181(28)
C(16)	4 683(24)	6 716(23)	−776(34)	101(19)	C(56)	5 415(20)	1 805(20)	5 794(29)	74(15)
C(17)	3 678(30)	6 247(31)	−1 251(44)	174(27)	C(57)	6 447(24)	1 876(24)	6 659(34)	110(21)
C(18)	4 863(25)	5 500(25)	−841(36)	169(22)	C(58)	5 958(22)	751(23)	6 118(32)	91(17)
C(19)	3 611(31)	5 962(32)	−596(47)	190(29)	C(59)	6 542(31)	1 783(31)	7 556(43)	160(30)
C(20)	4 963(34)	5 485(38)	−1 620(53)	259(38)	C(60)	6 312(29)	498(31)	5 589(43)	191(27)
C(21)	−719(20)	9 237(21)	3 303(30)	80(16)	C(61)	1 038(28)	8 173(29)	1 633(41)	129(27)
C(22)	−1 784(20)	9 427(22)	2 578(30)	99(16)	C(62)	904(44)	7 280(46)	2 384(62)	311(53)
C(23)	−1 138(18)	8 816(20)	1 764(28)	118(14)	C(63)	1 822(42)	7 890(44)	3 501(61)	314(44)
C(24)	−1 727(23)	10 126(24)	2 249(34)	108(20)	C(64)	1 080(34)	6 673(34)	2 307(47)	297(34)
C(25)	−1 428(22)	8 074(23)	1 830(33)	117(19)	C(65)	2 291(46)	7 952(47)	2 933(65)	295(52)
C(26)	1 672(18)	10 254(19)	4 134(28)	65(14)	C(66)	115(21)	10 552(21)	666(31)	98(17)
C(27)	1 953(27)	11 482(28)	4 262(39)	145(24)	C(67)	−885(29)	11 238(29)	743(42)	157(25)
C(28)	2 888(28)	10 458(29)	4 442(40)	249(25)	C(68)	216(35)	11 487(35)	−104(52)	194(33)
C(29)	2 039(41)	11 654(41)	3 407(57)	246(45)	C(69)	−1 289(37)	11 056(37)	−128(56)	203(38)
C(30)	3 088(31)	10 616(33)	5 414(45)	261(32)	C(70)	268(47)	11 839(47)	426(65)	206(55)
C(31)	843(20)	10 535(21)	6 464(30)	89(16)	C(71)	1 775(23)	8 706(25)	−830(34)	116(20)
C(32)	1 670(38)	11 305(38)	7 921(57)	250(39)	C(72)	2 388(20)	7 653(21)	−667(32)	101(16)
C(33)	451(31)	11 553(31)	6 711(44)	152(27)	C(73)	2 903(26)	8 870(27)	−364(39)	113(23)
C(34)	1 638(39)	11 509(40)	7 116(56)	244(39)	C(74)	2 435(30)	7 418(32)	244(46)	181(28)
C(35)	411(33)	12 098(34)	5 969(49)	196(31)	C(75)	3 260(26)	8 849(27)	−1 088(38)	112(22)
C(36)	649(22)	8 075(22)	6 057(33)	103(18)	C(76)	−785(20)	9 274(22)	−1 711(31)	85(17)
C(37)	−157(39)	7 163(39)	6 334(55)	175(38)	C(77)	−1 923(31)	8 682(34)	−2 845(46)	164(30)
C(38)	1 190(39)	7 030(39)	6 481(58)	258(41)	C(78)	−1 312(29)	9 649(31)	−3 234(42)	167(27)
C(39)	71(54)	6 963(51)	6 867(68)	374(63)	C(79)	−1 696(33)	8 192(34)	−3 245(48)	160(32)
C(40)	1 204(38)	6 682(38)	5 675(55)	202(37)	C(80)	−1 684(31)	10 166(33)	−2 924(45)	193(29)

* Anisotropic thermal factors are of the form: $\exp(-2\pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} h_i h_j a_i^* a_j^* U_{ij})$.

lengths and angles being attributed to packing effects. The mean La–S distance is 2.97 Å with a minimum and maximum deviation of −0.10 and 0.10 Å respectively. The 28 S–La–S angles within each polyhedron fall into four distinct groups: 59.6 (four), 84.9 (fourteen), 131.6 (eight), and 164.9° (two). The sixteen independent S–La–S chelate angles average to 59.6° with a minimum and maximum deviation of −1.0° and 1.4° respectively. In the crystal the sodium ions are situated just half-way between the anions forming infinite chains of positive and negative ions parallel to the *c* axis. The sodium ions have six nearest sulphur atoms, from two different anions, at distances varying from 2.81 to 3.58 Å, forming a highly distorted octahedron. Bond lengths and angles for the sixteen independent diethyldithiocarbamato-groups are comparable, within their rather large standard deviations, with analogous distances and angles from the literature.

The species $[Ln(Et_2dtc)_4]^-$, which occurs in the solid complexes, is also maintained in methyl cyanide solution, as is shown by the close similarity between solution and solid-state electronic spectra. Furthermore, the electrolytic conductances of the present complexes in methyl cyanide are strictly comparable with the values found for 1 : 1 electrolytes of similar type. Under the same conditions the molar conductance of $Na[Et_2dtc]$ is only about one third, indicating extensive ion-pair association. Hence, it is concluded that in MeCN any dissociation of the $[Ln(Et_2dtc)_4]^-$ species, into $Ln[Et_2dtc]_3$ and $[Et_2dtc]^-$, should not be extensive.

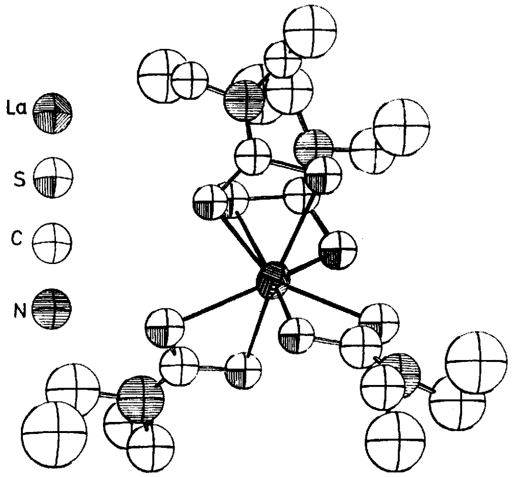

FIGURE 1 Structure of $Na[La(Et_2dtc)_4]$

I.r. Spectra.—The i.r. spectra of the $Na[Ln(Et_2dtc)_4]$ complexes exhibit the characteristic CN stretching vibration of diethyldithiocarbamates; this occurs at 1 472 cm^{-1} for the lanthanum compound and increases steadily to 1 484 cm^{-1} for the ytterbium compound. These rather low values are consistent with a high coordination number (1 510 ± 5 cm^{-1} and 1 496 ± 2 cm^{-1} for planar and octahedral complexes, respectively).[8] The band occurring at 981 cm^{-1} in $Na[Et_2dtc]$, which is assigned to a C=S stretching mode, is split for the present solid compounds into a doublet: 1 000—1 005 and 987—990 cm^{-1}. This is probably a solid-state splitting, since MeCN solutions of the lanthanum complex exhibit only one band at 1 000 cm^{-1}.

Spectral Properties.—Intraligand transitions. All complexes of the present series exhibit strong spectral absorptions above 27 kK with a maximum at 37.1—38.1 kK (ε *ca.* 50 000) and often a shoulder at *ca.* 34 kK. These bands are present in all the metal dithiocarbamato-complexes and have been attributed to intraligand transitions of the type $\pi\rightarrow\pi^*$.[9,10]

A definite shoulder is found in the spectra of the $[Ln(Et_2dtc)_4]^-$ ions: with $[La(Et_2dtc)_4]^-$, $\sigma_{sh} \simeq 29.6$ kK and ε *ca.* 500. Such a transition could be related to the band at 28.2 kK ($\varepsilon = 60$) of $Na[Et_2dtc]$, which has been assigned as an $n \longrightarrow \pi^*$ intraligand transition.[10]

4f–4f *Transitions.* In the spectral range 5—27.5 kK the present complexes from Pr to Yb, except Ce and Gd, exhibit a number of closely adjacent bands which are assigned as $4f$—$4f$ transitions. For each group of bands no analysis of its vibrational structure and ligand-field sublevels was attempted. Whenever possible, the baricentre of the intensity as well as the oscillator strength of each J level have been estimated for methyl cyanide solutions at room temperature. Such values and those of the molar absorbances of the most intense band within each group are given in Table 3.

When comparing the spectra of the present complexes with those of the corresponding aqua-ions or hexahalogeno-complexes a definite red shift is found for almost all the transitions. In most cases the frequency values increase according to the sequence $[Ln(Et_2dtc)_4]^- <$ $[LnI_6]^{3-}$ (ref. 11) $<$ $[LnBr_6]^{3-}$ (ref. 12) $<$ $[LnCl_6]^{3-}$ (ref. 12), $<$ $[Ln(H_2O)_9]^{3+}$, which parallels the well-known nephelauxetic series.[13] Within the $4f$ shell, the nephelauxetic effect is rather small and decreases as the atomic number increases.[13] For the present Et_2dtc complexes the ratios between the baricentres of corresponding J levels of the complex and the free ion [14] are not true nephelauxetic ratios since no allowance for the small ligand-field effect on both the ground- and excited-levels of the complex is being made (pseudo-nephelauxetic ratio). Nevertheless, both effects are expected to be reduced by taking the average value β^{4f} of these pseudo-nephelauxetic ratios only for the higher frequency bands (*viz.* for the band in the range 15—27 kK).

For some praseodymium and erbium complexes one

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TABLE 3

Spectral data for internal 4*f* transitions of $Na[Ln(Et_2dtc)_4]$

Compound	Excited level	σ_J [a]	$P \times 10^6$ [b]	$\varepsilon_{max.}$ [c]
$Na[Pr(Et_2dtc)_4]$	$^3F_2$ [d]	5.01		9.5
	$^3F_3$	6.24	11.67	7.0
	$^3F_4$	6.76	5.94	4.9
	$^1G_4$	9.67	0.44	0.4
	$^1D_2$	16.42	4.17	3.0
	$^3P_0$	20.02	3.87	2.9
	$^3P_1,{}^1I_6$	[20.64]	16.07	6.0
	$^3P_2$	21.75	21.15	14.5
$Na[Nd(Et_2dtc)_4]$	$^4F_{3/2}$	11.26	3.80	3.2
	$^4F_{5/2},{}^2H_{9/2}$	[12.32]	12.89	14.9
	$^4F_{7/2},{}^4S_{3/2}$	[13.24]	13.71	12.3
	$^4F_{9/2}$	14.51	1.03	1.0
	$^2H_{11/2}$	15.81	0.38	0.4
	$^4G_{5/2}$ [d], $^2G_{7/2}$	[16.83]	105.0	88.8
	$^2H_{13/2},{}^4G_{7/2}$	18.71	19.98	12.0
	$^4G_{9/2}$	19.20		4.0
	$^2K_{15/2},{}^2G_{9/2}$, $(^2D,{}^2P)_{3/2}$	20.82	3.56	1.2
	$^4G_{11/2}$	21.40		0.8
	$^2P_{1/2}$	22.96	1.20	2.4
	$^2D_{5/2}$	23.55		
$Na[Sm(Et_2dtc)_4]$	$^6F_{1/2}$ [d], $^6H_{15/2}$	6.21	4.68	4.3
	$^6F_{3/2}$ [d]	6.53	6.76	7.3
	$^6F_{5/2}$	7.05	7.15	8.1
	$^6F_{7/2}$	7.89	7.13	7.2
	$^6F_{9/2}$	9.10	3.92	5.9
	$^6F_{11/2}$	10.40	0.63	0.7
	$^4F_{3/2}$	18.76	0.23	0.2
	$^4G_{7/2}$	19.89	0.19	0.2
	$^4I_{9/2},{}^4M_{15/2}$	20.60	2.93	1.3
	$^4I_{11/2}$			
	$^4I_{13/2}$	21.38	1.35	1.0
	$^4F_{5/2}$	21.99		0.3
	$^4M_{17/2},{}^4G_{9/2}$, $^4I_{15/}2$	22.50	0.81	0.3
	?	23.24	10.44	8.1
	?	23.86	35.46	36.0
	?	25.66	24.43	26.4
$Na[Eu(Et_2dtc)_4]$ [e]	$^7F_6$	4.85		
	$^5D_0$	16.91		
		17.07		
		17.23		
		17.39		
		17.59		
		17.65		
	$^3D_1$ [d]	18.63		
	$^5D_2$	21.43		23.0
	$^5D_3$	24.34		7.0
	$^5L_6$	25.20		9.0
$Na[Tb(Et_2dtc)_4]$	$^7F_2$	4.92		1.8
	$^5D_4$	20.42	0.21	0.3
$Na[Dy(Et_2dtc)_4]$	$^6H_{9/2},{}^6F_{11/2}$ [d]	7.67	25.36	13.1
	$^6F_{9/2},{}^6H_{7/2}$	8.96	4.56	2.6
	$^6H_{5/2}$	10.20		0.2
	$^6F_{7/2}$	10.86	3.31	3.1
	$^6F_{5/2}$	12.23	1.69	2.1
	$^6F_{3/2}$	13.02	0.67	0.6
	$^4F_{9/2}$	20.99	0.44	0.2
	$^4I_{15/2}$	21.91	1.50	1.3
	$^4G_{11/2}$	23.16	0.59	0.6
$Na[Ho(Et_2dtc)_4]$	$^5I_6$	8.58	1.51	1.7
	$^5I_5$	11.15	0.32	0.4
	$^5I_4$	13.28		
	$^5F_5$	15.30	5.96	5.0
	$^5S_2,{}^5F_4$	14.33	6.92	5.6
	$^5F_3$	20.39	2.04	2.4
	$^5F_2$	20.84	1.20	1.3
	$^3K_8$	21.16	3.00	3.4
	$^5G_6$ [d], $^5F_1$	21.82	108.5	83.2
	$(^5G,{}^3G)_5$	23.59	9.95	8.6
	$^5G_4$	25.51	1.35	
	$^3K_7$	25.97	1.94	
	$(^5G,{}^3H)_5,{}^3H_6$, [d] $(^5F,{}^3F,{}^5G)_2$	27.45	66.95	
$Na[Er(Et_2dtc)_4]$	$^4I_{13/2}$	6.56	3.00	2.9
	$^4I_{11/2}$	10.17	1.57	2.1
	$^4I_{9/2}$	12.43	0.92	1.0
	$^4F_{9/2}$	15.16	5.78	5.0
	$^4S_{3/2}$	18.28	1.42	1.2
	$(^2H,{}^{d4}G)_{11/2}$	18.94	40.35	30.0
	$^4F_{7/2}$	20.34	4.14	5.5
	$^4F_{5/2}$	21.98	1.70	1.6
	$^4F_{3/2}$	22.40		0.8
	$(^2G,{}^4F,{}^2H)_{9/2}$	24.38	1.26	1.3
	$^4G_{11/2}$ [d]	26.07	77.38	59.3
	$^4G_{9/2}$	27.09		
$Na[Tm(Et_2dtc)_4]$	$^3H_5$	8.24	5.19	5.4
	$^3H_4$ [d]	12.48	14.01	10.9
	$^3F_3$	14.34	10.65	9.8
	$^3F_2$	14.87	1.00	0.6
	$^1G_4$ [d]	21.16	7.09	3.7
	$^1D_2$	27.39	sh	sh
$Na[Yb(Et_2dtc)_4]$	$^2F_{5/2}$	10.16	18.90	14.5

[a] σ_J is the wavenumber in kK of the intensity baricentre of the band group corresponding to the excited *J* level indicated. [b] Oscillator strengths calculated as $P = 4.318 \times 10^{-9}\int\varepsilon(\sigma)d\sigma$. [c] $\varepsilon_{max.}$ is the molar extinction coefficient of the highest band of each group in the methyl cyanide solution absorption spectra; the wavenumber of this band does not necessarily coincide with σ_J. [d] Hypersensitive transition. [e] The reported frequencies are for single narrow peaks superposed on the broad electronic transfer band. The values of ε are estimated by subtracting the absorbance of the main band.

TABLE 4

Spectral data for some complexes of cerium(III), europium(III), and ytterbium(III)

Complex	σ	ε	δ
$[Ce(Et_2dtc)_4]^-$	22.8 (25.6) [a]	340 (120) [a]	1.3 (1.2) [a]
$[CeCl_6]^{3-}$ [12]	30.3	1 600	0.8
$[CeBr_6]^{3-}$ [12]	29.15	1 600	1.0
$[Eu(Et_2dtc)_4]^-$	23.8	470	3.3
$[EuCl_6]^{3-}$ [12]	33.2	400	2.1
$[EuBr_6]^{3-}$ [12]	24.5	250	2.0
$[EuI_6]^{3-}$ [11]	14.8		
$[Yb(Et_2dtc)_4]^-$	25.15	185	2.0
$[YbCl_6]^{3-}$ [12]	36.7	160	1.7
$[YbBr_6]^{3-}$ [12]	29.2	105	2.4
$[YbI_6]^{3-}$ [11]	17.85		

[a] Estimated value from Gaussian analysis.

obtains the following pseudo-$\bar{\beta}^{4f}$ values: $[Pr(H_2O)_9]^{3+}$, 0.968;[14] $[PrCl_6]^{3-}$, 0.962;[12] $[PrBr_6]^{3-}$, 0.956;[12] $[Pr(Et_2dtc)_4]^-$, 0.939; $[Er(H_2O)_9]^{3+}$, 1.002;[14] $[ErCl_6]^{3-}$, 0.999;[12] $[ErBr_6]^{3-}$, 0.998;[12] $[ErI_6]^{3-}$, 0.996;[11] $[Er(Et_2dtc)_4]^-$, 0.995.

The oscillator strengths of 4*f*→4*f* transitions for these lanthanoid diethyldithiocarbamates are usually 2—3 times higher than those of the corresponding aqua-ions. For the hypersensitive transitions,[15] however, oscillator strengths rise to 7—20 times those of the aqua-ions.

Visible Spectra of the Europium and Ytterbium Dithiocarbamates.—The present diethyldithiocarbamato complexes of europium(III) and ytterbium(III) exhibit, in MeCN, a rather broad and intense absorption band at 23.8 and 25.15 kK, respectively (Table 4 and Figure 2). In the reflectance spectra of these solid compounds the bands are at 23.0 and 25.0 kK, respectively.

Because of their characteristics of intermediate intensity and large half-width these bands are assigned

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[15] R. D. Peacock, *Structure and Bonding*, 1975, **22**, 83.

as electron-transfer transitions from the filled π orbitals of the ligands to the $4f$ orbitals of the metal ion. In Table 4 the spectral features of these bands for [Eu(Et$_2$dtc)$_4$]$^-$ and [Yb(Et$_2$dtc)$_4$]$^-$ are compared with those for the halogeno-complexes of the same elements.

The frequencies of these $\pi \rightarrow 4f$ transitions in dithiocarbamates are only slightly lower than those for the corresponding bromo-complexes. This settles the value of the optical electronegativity {calculated according to the equation $\sigma = [\chi_{opt}(L) - \chi_{opt}(M)]30$ kK}[16] for [Et$_2$dtc]$^-$ at *ca.* 2.7 (2.8 for Br$^-$)[16] with lanthanoids, a somewhat higher value than the previously reported values of 2.5—2.6.[3,17]

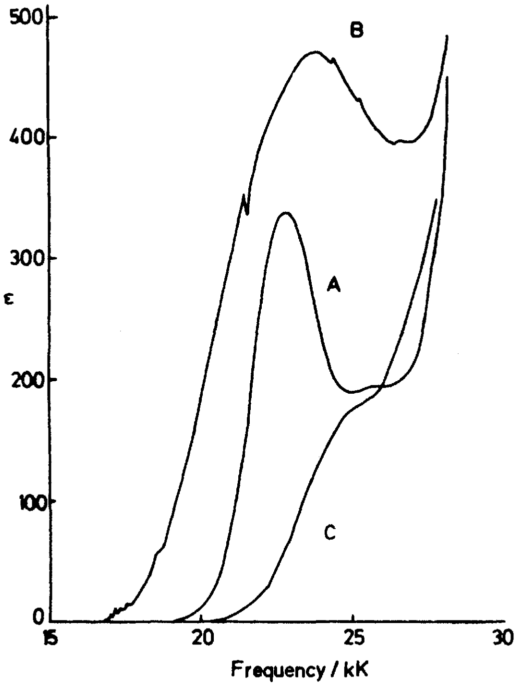

FIGURE 2 Absorption spectra of some Na[Ln(Et$_2$dtc)$_4$] compounds in methyl cyanide solution: Ln is Ce(A), Eu(B), and Yb(C)

For the complexes of the remaining lanthanoids, which are less easily reducible than europium(III) and ytterbium(III), such transitions are expected to fall at higher frequencies, *i.e.* in the spectral region obscured by the stronger intraligand transitions.

Visible Spectrum of [Ce(Et$_2$dtc)$_4$]$^-$.—The yellow cerium(III) complex exhibits one absorption band at 22.8 kK of moderate intensity and half-width (Table 4 and Figure 2). A second band is also present as a shoulder at 25.6 kK (ε *ca.* 195) on the low-frequency side of the steeply rising intraligand bands. Gaussian analysis suggests values of ε 120 and $\delta(-)$ 1.2 kK for this second band.

Two alternative assignments can be given for these transitions: $4f \rightarrow 5d$ transitions or inverted electron-transfer transitions.

According to the first assignment, the two bands are attributed to electron transition from the ground state $^2F_{5/2}$ ($4f^1$) to the lowest ligand-field components originating from the $^2D_{3/2,5/2}$ ($5d^1$) levels. Such an assignment is supported by the small value of the halfwidths of these bands, a feature which is considered to be characteristic of intershell transitions, as contrasted with electron-transfer transitions.[3] It may be recalled, however, that genuine $4f \rightarrow 5d$ transitions occur at substantially higher frequencies in known cerium(III) compounds such as 29.15 for [CeBr$_6$]$^{3-}$ (ref. 12), 30.30 for [CeCl$_6$]$^{3-}$ (ref. 12), and 33.7 kK for [Ce(H$_2$O)$_9$]$^{3+}$ (ref. 18). For [Ce(Et$_2$dtc)$_4$]$^-$ this assignment should require simultaneously a large $5d$-orbital splitting and a large decrease in the $^2D_{3/2,5/2}$–$^2F_{5/2}$ term separation, compared with the free ion. This is not unreasonable in view of the position of Et$_2$dtc$^-$ in the spectrochemical [Br$^-$ < Cl$^-$ < Et$_2$dtc$^-$ < H$_2$O] and nephelauxetic [(EtO)$_2$PSe$_2^-$ < Et$_2$dtc$^-$ < (EtO)$_2$PS$_2^-$ < Br$^-$ < Cl$^-$ < H$_2$O] series.[13,19] As a rough estimate of the nephelauxetic effect on $5d$ orbital energy, one could make use of the Jørgensen relationship $(1 - \beta_L^M) = h(L) \times k(CI)$ where β_L^M is the nephelauxetic ratio of the term energies in the complex relative to the free ion, and h and k are factors characteristic of the ligands (L) and central ion (CI), respectively. The factors h are 1.0 for H$_2$O and 2.8—3.0 for [Et$_2$dtc]$^-$.[19] The empirical relationship holds for terms belonging to the same subshell configuration and is here tentatively assumed to be valid for terms of different subshell configurations, too. Taking the average energies of $5d$ orbitals relative to the $^3F_{5/2}$ ground state to be 44.7 kK in [Ce(H$_2$O)$_9$]$^{3+}$ and 51.23 kK in the free Ce^{3+} ion,[20] one obtains $\beta_{H_2O}^{Ce,5d}$ 0.87, k(Ce^{III},$5d$) 0.13, and $\beta_{Et_2dtc}^{Ce,5d}$ 0.64—0.61. The average energy of the $^2D(5d)$ term in [Ce(Et$_2$dtc)$_4$]$^-$ is then estimated to be 32.8—31.2 kK, *i.e.* 11.9—13.5 kK lower than for the cerium(III) aqua-ion. Since the splitting effect on the partly filled d shell for [Et$_2$dtc]$^-$ is *ca.* 90% of that for H$_2$O,[19] the lowest one of the $4f \rightarrow 5d$ transitions could be expected to fall at frequencies as low as *ca.* 21—23 kK in [Ce(Et$_2$dtc)$_4$]$^-$, consistent with the assignment of the two bands at 22.8 and 25.6 kK.

Otherwise, in spite of their small halfwidths, these bands could be assigned as inverted electron-transfer transitions from a $4f$ metal orbital to empty π^* molecular orbitals of the ligands. Transitions of this type have been suggested for a number of cerium(III) compounds such as cerium polytungstate or phenanthroline complexes. Of course, this kind of electron transfer (oxidation of the central-metal ion) is only expected to occur at the lowest energy for the most easily oxidizable lanthanoid(III) ion, *i.e.* for cerium(III).

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