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Polynuclear Complexes of 3d and 4f Transition Metals. Synthesis and Structure of Lanthanide(III) Adducts with Copper and Nickel Schiff's Base Complexes as Ligands

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Abstract

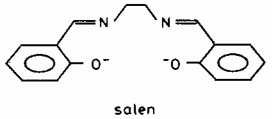
The synthesis and characterization of trinuclear complexes containing both 3d and 4f metal ions is presented: $Ln(NO_3)_3[Cu(salpn)]_2$ (Ln = Eu, Dy) and $Ln(NO_3)_3[Ni(salpn)(pn)]_2 \cdot 2H_2O$ (Ln = La–Lu). The crystal and molecular structure of $Ce(NO_3)_3[Cu(salpn)]_2 \cdot CH_3NO_2$ has been determined by single-crystal X-ray diffraction. The complex forms orthorhombic crystals, space group *Fdd*2 (ITC No 43), a = 19.479(2), b = 26.980(2), c = 30.698(2) Å, Z = 16. The structure was solved by Patterson and Fourier techniques and refined by least squares to a final conventional $R_F = 0.045$ ($R_W = 0.052$). The Ce(III) ion is 10-coordinate, with an irregular coordination polyhedron. This polyhedron may be best described as a trigonal bipyramidal arrangement of five bidentate ligands, two axial nitrates, one equatorial nitrate and two equatorial [Cu(salpn)] ligands. The average Ce–O bond length is 2.53(10) Å. The two Cu(II) ions form distorted octahedral CuN_2O_4 and square-based pyramidal CuN_2O_3 chromophores, respectively. A molecule of nitromethane links pairs of complex molecules, related by a twofold axis, into dimers. Cell parameters could also be determined for $Sm(NO_3)_3[Cu(salpn)]_2$: a = 10.309(2), b = 14.768(2), c = 10.998(1) Å. The nickel complexes form an isomorphous series and their structure is discussed on the basis of spectroscopic data and of comparison with the copper complexes.

Introduction

Interest in polynuclear complexes is stimulated by the role they play in a number of different areas, *e.g.* heterogeneous catalysis, the design of magnetic materials, bioinorganic chemistry. Coupled polynuclear systems containing 3d elements are being extensively investigated [1] but only a few heterobinuclear and trinuclear complexes, derived from Schiff's base reagents, that contain both 3d metal ions and either 5f (uranyl or Th(IV)) [2] or 4f ions [3–4] have been reported. In an attempt to gain more information on the properties of the lanthanide polynuclear complexes, we have developed a research program dealing with both 4f–4f and 3d–4f complexes. As a starting point, we opted for the use of Schiff's base derivatives as ligands. Both the un-ionized and the ionized form of these bases are indeed known to form stable complexes with lanthanide salts, having various metal:ligand ratios, 1:1, 1:2, 1:3 and 2:3 [5–7]; for these latter, a dinuclear structure has been postulated [5]. Finally, a very recent article presents various chemical, physico-chemical and spectroscopic properties of polynuclear complexes of lanthanide salts with nickel and copper Schiff's bases [8].

In this communication, we present the synthesis and characterization of two series of trinuclear complexes: $Ln(NO_3)_3[Cu(salpn)]_2$ and $Ln(NO_3)_3[Ni(salpn)(pn)]_2 \cdot 2H_2O$, where salpn stands for the ionized form of N,N'-propylenebis(salicylideneimine) and pn for 1,3-diaminopropane. We also report the crystal and molecular structure of the cerium(III) complex $Ce(NO_3)_3[Cu(salpn)]_2 \cdot CH_3NO_2$**.

salpn



salen

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**Systematic name: bis(copper)tris(nitrato)(nitromethanato)[μ-[2,2'-[1,3-propanediyl bis(nitrolomethylidyne)]bis(phenolato)](2-)-N,N',O,O':O,O']]cerium(III).

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Experimental

Syntheses of the Nickel Complexes

The nickel-containing ligand, [Ni(salpn)(pn)] was prepared as reported by Holm [9] by treating a suspension of nickel salicylate with a twofold mole excess of 1,3-diaminopropane in alcohol, at reflux temperature. This ligand could also be prepared by treating [Ni(salpn)] with 1 mol equivalent of 1,3-diaminopropane in alcohol. The apple green suspension gradually became green brown and most of the solids dissolved. The solution was filtered, evaporated to small bulk and on cooling a brown crystalline precipitate was obtained. (*Anal.* Found C, 57.9%; H, 6.8%; N, 13.4%. Calculated for $C_{20}H_{26}N_4O_2Ni$: C, 58.1%; H, 6.45%; N, 13.6%). This complex (0.90 g, 2.2 mmol) was dissolved in 50 ml warm alcohol to give a brown solution to which a filtered solution of the lanthanide nitrate hydrate (1 mmol in 10 ml alcohol) was added. The resultant pale green solution was stirred and allowed to cool whereupon a very fine precipitate formed. The product was collected and washed with a little cold alcohol, ether, and air dried. The complexes $Ln(NO_3)_3[Ni(salpn)(pn)]_2 \cdot 2H_2O$ were prepared for Ln = La–Lu, except Pm.

Selected analytical data are reported in Table I. The complexes are stable in the solid state, are soluble in most polar organic solvents but slowly decompose in solution; they decompose rapidly in water; attempts to recrystallize them from various solvents always resulted in the formation of amorphous yellow solids.

Synthesis of the Copper Complexes

These complexes were synthesized as previously described for Ln = La–Sm [3]. For Eu, both di- and trinuclear complexes were obtained and a trinuclear complex was also isolated for Dy. Analytical data are reported in Table I.

Crystal Structure Determination

The $Ln(NO_3)_3[Cu(salpn)]_2$ complexes are stable in both the solid and solution state; they can be recrystallized from alcohol but the crystals obtained rapidly deteriorate when removed from the solvent. Crystals of $Sm(NO_3)_3[Cu(salpn)]_2$ obtained from methanol were sufficiently stable to yield the following crystal parameters: a = 10.309(2), b = 14.768(2), c = 10.988(1) Å, and β = 94.45(1)°; probable space group is $P21/a$. However, no data collection could be carried out. Fine dark green crystals of $Ce(NO_3)_3[Cu(salpn)]_2 \cdot CH_3NO_2$ were grown by slowly cooling an almost saturated solution of the complex in nitromethane. A crystal of approximate dimensions 0.25 × 0.25 × 0.3 mm was selected. Data were collected on a Syntex $P2_1$ diffractometer for $0 < 2\theta < 110°$ using CuKα (λ = 1.5418 Å), with a variable scan speed 3–29.3°/min depending on the intensity of a 2s prescan, and with a scan range of ±1° around the Kα_1–Kα_2 angles. Of the 2501 reflexions collected, 2 were rejected (0,2,2 and 2,0,2: intensity too high), and 2429 were considered observed ($I/\sigma(I) > 3\sigma(I)$). The intensity of three standard reflexions were measured every 200 reflexions and showed a very slight systematic variation during the data collection, for which a correction was made. The data were also corrected for absorption (μ = 10.2 cm^{-1}), Lorentz and polarization effects. The transmission range was 0.77–0.84.

The systematic absences h, k, l: $h + k, k + l, (h + l) \neq 2n$ and $0,k,l$: $k + l \neq 4n$, and $h, 0, l$: $h + l \neq 4n$ uniquely determine the space group as $Fdd2$. The position of the cerium atom was determined from a Patterson synthesis at approximately x = 0.26, y = 0.2 with z arbitrarily fixed at zero. A least squares refinement on this position enabled the determination of the positions of the two Cu atoms and several O atoms about the Ce atom. Subsequent alternate structure factor calculations

TABLE I. Selected Analytical Data for $Ln(NO_3)_3[Cu(salpn)]_2$ and $Ln(NO_3)_3[Ni(salpn)(pn)]_2 \cdot 2H_2O$.

M	Ln	% C		% H		% N	
		found	calcd.	found	calcd.	found	calcd.
Cu	Eu[a]	39.76	39.78	3.20	3.14	9.24	9.56
	Dy	39.28	39.41	3.18	3.11	9.07	9.46
Ni	Ce	40.06	40.42	4.40	4.75	12.61	12.96
	Nd	40.59	40.28	4.97	4.73	12.93	12.92
	Sm[b]	40.08	40.08	4.71	4.71	12.65	12.85
	Eu	40.31	40.03	4.48	4.70	12.75	12.84
	Dy	39.83	39.68	4.41	4.66	12.52	12.72

[a] % Eu found 21.03, calcd. 21.17. [b] % Sm found 12.75, calcd. 12.88.

and difference Fourier syntheses revealed the positions of all the remaining non-H atoms. The structure was then refined in large blocks with anisotropic temperature factors, a contribution from the calculated H atoms (salpn ligand) with fixed isotropic temperature factors, and the application of an empirical weighting scheme giving decreased weight to reflexions with high and low F_{obs} and high $\sin\theta/\lambda$. The structure refinement converged to a final conventional $R_F = 0.045$ ($R_W = 0.052$). Residual peaks in the final difference Fourier synthesis lay in close proximity to the Ce and Cu atoms and one of the nitrate groups. Two CH_3NO_2 molecules lie with their carbon and nitrogen atoms on a twofold axis (special position 8(a)). A refinement was tried with the molecule of the opposite hand, but this had slightly less good final R_F and showed less consistent bond lengths and angles. All calculations were carried out using the XRAY-72 programs [10]. Atomic scattering factors for neutral atoms were taken from Cromer and Mann [11] and dispersion corrections for Ce and Cu were calculated by Cromer and Liberman [12]. The list of atomic positional and isotropic thermal parameters is presented in Table II and Table III contains selected bond lengths and bond angles.

TABLE II. Fractional Atomic Coordinates (×10^4) and Isotropic Temperature Factors (×10^2) for $Ce(NO_3)_3[Cu(salpn)]_2$, with e.s.d.s in Parentheses.

Atom	*x*	*y*	*z*	*U*(EQ.)
Ce	2600.5(3)	256.2(2)	0	3.73(2)
Cu(1)	3591(1)	−282(1)	744.2(8)	6.09(9)
Cu(2)	1570(1)	−195.0(9)	−749.8(8)	6.06(8)
O(11)	3255(5)	−486(4)	181(4)	6.1(4)
O(12)	3720(5)	332(4)	427(3)	6.0(4)
O(21)	1634(7)	457(4)	−451(4)	7.6(5)
O(22)	1854(5)	−436(4)	−159(3)	5.3(4)
O(31)	2580(6)	1094(4)	371(4)	6.5(4)
O(32)	2785(8)	1119(5)	−310(4)	7.6(5)
O(33)	2739(8)	1809(4)	69(5)	9.7(6)
O(41)	1512(5)	379(5)	524(3)	5.9(4)
O(42)	2403(8)	111(6)	820(4)	7.9(5)
O(43)	1546(7)	226(6)	1218(5)	9.2(6)
O(51)	3545(9)	236(8)	−1250(5)	12.1(8)
O(52)	3470(10)	330(10)	−606(6)	17(1)
O(53)	2700(10)	−13(9)	−836(8)	16(1)
O(61)	200(10)	361(8)	3971(9)	18(1)
O(71)	2160(10)	2209(8)	2010(10)	18(1)
N(11)	3309(8)	−905(6)	1008(5)	7.7(6)
N(12)	3997(8)	25(6)	1272(4)	7.5(6)
N(21)	1280(7)	145(6)	−1293(4)	6.6(5)
N(22)	1587(8)	−867(6)	−970(5)	7.6(6)
N(31)	2684(7)	1358(4)	17(6)	6.7(4)
N(41)	1820(6)	258(5)	867(5)	5.3(5)
N(51)	3257(8)	158(6)	−942(6)	6.8(6)
N(61)	0	0	4147(9)	9(1)
N(71)	2500	2500	2210(10)	14(2)
C(11)	3281(8)	−956(6)	50(9)	7.1(7)
C(12)	3350(10)	−1051(9)	−414(8)	10(1)
C(13)	3340(20)	−1533(9)	−560(10)	11(1)
C(14)	3260(20)	−1915(9)	−280(10)	13(1)
C(15)	3210(10)	−1844(9)	150(10)	11(1)
C(16)	3250(10)	−1356(9)	328(9)	8.9(9)
C(17)	3170(10)	−1297(8)	788(9)	9(1)
C(18)	3180(20)	−960(10)	1490(10)	13(1)
C(19)	3220(20)	−500(10)	1705(7)	12(1)
C(110)	3930(20)	−220(10)	1691(7)	12(1)
C(111)	4280(10)	458(9)	1279(6)	8.1(8)
C(112)	4422(8)	772(7)	933(5)	5.8(6)
C(113)	4860(10)	1178(9)	1002(6)	8.0(8)
C(114)	5060(10)	1490(10)	662(9)	10(1)
C(115)	4790(10)	1407(9)	266(7)	8.8(8)
C(116)	4337(9)	1039(8)	191(6)	7.4(7)
C(117)	4146(7)	697(7)	506(5)	5.6(6)
C(21)	1184(8)	817(6)	−532(6)	5.7(6)
C(22)	1040(10)	1151(8)	−194(7)	8.0(8)
C(23)	590(10)	1541(9)	−285(8)	9.6(9)
C(24)	270(10)	1599(9)	−694(8)	9.0(9)
C(25)	446(9)	1280(8)	−1015(7)	7.4(7)
C(26)	882(9)	885(7)	−940(6)	6.3(6)
C(27)	1017(9)	559(7)	−1302(6)	6.9(7)
C(28)	1380(20)	−150(10)	−1732(7)	12(1)
C(29)	1190(20)	−620(10)	−1718(8)	12(1)
C(210)	1650(20)	−960(10)	−1454(8)	11(1)
C(211)	1520(10)	−1253(8)	−737(8)	9.5(9)
C(212)	1480(10)	−1264(7)	−243(7)	7.0(7)
C(213)	1300(10)	−1706(7)	−50(8)	8.2(8)
C(214)	1240(10)	−1761(8)	390(10)	9(1)
C(215)	1410(10)	−1350(9)	641(7)	8.5(9)
C(216)	1610(10)	−920(7)	459(7)	7.4(8)
C(217)	1654(8)	−853(6)	14(7)	5.8(5)
C(61)	0	0	4590(10)	15(2)
C(71)	2500	2500	2720(10)	18(3)
H(12)	3449	−759	−616	7
H(13)	3359	−1594	−902	7
H(14)	3241	−2252	−394	7
H(15)	3153	−2137	361	7
H(17)	2988	−1595	971	7
H(181)	2661	−1084	1543	7
H(182)	3465	−1216	1640	7
H(191)	2891	−291	1569	7
H(192)	3097	−575	2020	7
H(1101)	3972	−27	1958	7
H(1102)	4314	−511	1723	7
H(111)	4434	584	1577	7
H(113)	5030	1252	1307	7
H(114)	5408	1774	718	7
H(115)	4943	1621	−1	7
H(116)	4093	1016	−104	7
H(22)	1284	1119	101	7
H(23)	468	1794	−48	7
H(24)	−61	1872	−784	7
H(25)	246	1334	−1316	7
H(27)	887	708	−1606	7

(continued overleaf)

TABLE II *(continued)*

Atom	*x*	*y*	*z*	*U*(EQ.)
H(211)	1513	−1600	−878	7
H(213)	1195	−2004	−246	7
H(214)	1070	−2078	533	7
H(215)	1384	−1390	973	7
H(216)	1734	−621	665	7
H(281)	1075	32	−1969	7
H(282)	1857	−120	−1831	7
H(291)	711	−662	−1539	7
H(292)	1084	−785	−2003	7
H(2101)	1581	−1320	−1543	7
H(2102)	2139	−869	−1566	7

Crystal Data

$C_{35}H_{35}N_8O_{15}CeCu_2$, MW = 1074.91, orthorhombic, a = 19.479(2), b = 26.980(2), c = 30.698(2) Å, U = 16133(2) Å^3, $d_{(obsd)}$ = 1.78(6), $d_{(calcd)}$ = 1.779 g cm^{-3} at 293 K, Z = 16. Space group *Fdd*2 (ITC No. 43).

Other Measurements

IR spectra were measured as Nujol mulls by using a Perkin-Elmer 577 spectrometer. Reflectance spectra were recorded on a Perkin-Elmer-Hitachi spectrometer, model 340 equipped with a R 10-A integrating sphere. X-ray powder diffraction diagrams were obtained by using CuKα, a Guinier camera and a Philips PW 1729 generator.

TABLE III. Selected Bond Lengths (Å) and Angles (°) for $Ce(NO_3)_3[Cu(salpn)]_2 \cdot CH_3NO_2$, with e.s.d.s in Parentheses[a].

Ce–O(11)	2.43(1)	Ce–O(32)	2.54(1)
Ce–O(12)	2.55(1)	Ce–O(41)	2.68(1)
Ce–O(21)	2.40(1)	Ce–O(42)	2.58(1)
Ce–O(22)	2.42(1)	Ce–O(52)	2.52(2)
Ce–O(31)	2.53(1)	Ce–O(53)	2.68(3)
Cu(1)–O(11)	1.93(1)	Cu(2)–O(21)	1.99(1)
Cu(1)–O(12)	1.94(1)	Cu(2)–O(22)	2.01(1)
Cu(1)–N(11)	1.94(2)	Cu(2)–N(21)	1.99(1)
Cu(1)–N(12)	1.98(1)	Cu(2)–N(22)	1.93(7)
Cu(1)–O(42)	2.56(2)	Cu(2)–O(53)	2.28(2)
		Cu(2)–O(71)	2.54(2)
O(11)–Cu(1)–O(12)	80.6(5)	O(12)–Cu(1)–N(12)	90.2(6)
O(11)–Cu(1)–N(11)	91.8(6)	O(12)–Cu(1)–O(42)	79.0(4)
O(11)–Cu(1)–N(12)	170.6(6)	N(11)–Cu(1)–N(12)	97.6(7)
O(11)–Cu(1)–O(42)	83.8(4)	N(11)–Cu(1)–O(42)	93.7(6)
O(12)–Cu(1)–N(11)	169.9(6)	N(12)–Cu(1)–O(42)	96.5(5)
O(21)–Cu(2)–O(22)	81.5(5)	O(22)–Cu(2)–O(71)	87.0(7)
O(21)–Cu(2)–N(21)	89.8(6)	N(21)–Cu(2)–N(22)	98.3(6)
O(21)–Cu(2)–N(22)	171.6(6)	N(21)–Cu(2)–O(53)	94.5(8)
O(21)–Cu(2)–O(53)	78.6(7)	N(21)–Cu(2)–O(71)	92.2(8)
O(21)–Cu(2)–O(71)	90.4(7)	N(22)–Cu(2)–O(53)	98.3(8)
O(22)–Cu(2)–N(21)	171.3(5)	N(22)–Cu(2)–O(71)	91.6(7)
O(22)–Cu(2)–N(22)	90.4(6)	O(53)–Cu(2)–O(71)	167.1(9)
O(22)–Cu(2)–O(53)	84.7(7)		

Nitrate groups

N(31)–O(31)	1.31(2)	N(41)–O(41)	1.25(2)	N(51)–O(51)	1.12(3)
N(31)–O(32)	1.21(2)	N(41)–O(42)	1.21(2)	N(51)–O(52)	1.20(3)
N(31)–O(33)	1.23(2)	N(41)–O(43)	1.21(2)	N(51)–O(53)	1.22(3)

O(31)–N(31)–O(32)	115(1)	Ce–O(31)–N(31)	96.4(9)
O(31)–N(31)–O(33)	116(2)	Ce–O(32)–N(31)	99(1)
O(32)–N(31)–O(33)	128(2)		
O(41)–N(41)–O(42)	116(1)	Ce–O(41)–N(41)	95.3(8)
O(41)–N(41)–O(43)	124(1)	Ce–O(42)–N(41)	102(1)
O(42)–N(41)–O(43)	120(1)	Cu(1)–O(42)–N(41)	174(1)
O(51)–N(51)–O(52)	119(2)	Ce–O(52)–N(51)	112(2)
O(51)–N(51)–O(53)	138(2)	Ce–O(53)–N(51)	103(2)
O(52)–N(51)–O(53)	103(2)	Cu(2)–O(53)–N(51)	166(2)

(continued on facing page)

TABLE III *(continued)*

Schiff's base			
N(11)–C(17)	1.28(3)	O(11)–C(11)	1.33(2)
N(12)–C(111)	1.29(2)	O(11)–C(117)	1.31(2)
N(21)–C(27)	1.27(3)	O(21)–C(21)	1.33(2)
N(21)–C(211)	1.23(2)	O(22)–C(217)	1.30(2)
Torsion angles in the tris(methylene) group			
N(11)–C(18)–C(19)–C(110)	61	C(18)–C(19)–C(110)–N(12)	79
N(21)–C(28)–C(29)–C(210)	70	C(28)–C(29)–C(210)–N(22)	70
Nitromethane			
N(61)–O(61)	1.18(3)	O(61)–N(61)–O(61)′	125(3)
N(61)–C(61)	1.37(5)	O(61)–N(61)–C(61)	117(2)
N(71)–O(71)	1.21(3)	O(71)–N(71)–O(71)″	116(4)
N(71)–C(71)	1.56(6)	O(71)–N(71)–C(71)	122(2)

[a] ′ Denotes symmetry operation $-x, -y, z$ and ″ denotes $0.5 - x, 0.5 - y, z$.

Results and Discussion

The Copper Complexes

The isolation of dinuclear complexes Ln(NO$_3$)$_3$-[Cu(salpn)]•2H$_2$O is reported for Ln = Eu–Lu, whereas trinuclear complexes Ln(NO$_3$)$_3$[Cu(salpn)]$_2$ form with Ln = La–Sm [3]. The dinuclear complexes we prepared were not completely pure and always appeared to contain some of the trinuclear complexes, even if synthesized in the presence of an excess of lanthanide nitrate. For Ln = Eu, both di- and trinuclear complexes were isolated and a trinuclear complex was also obtained for Ln = Dy. X-ray powder photographs indicate that the complexes with Ln = Ce–Eu are isostructural whereas the dysprosium complex has a different structure.

A crystallographic study of Ce(NO$_3$)$_3$[Cu-(salpn)]$_2$•CH$_3$NO$_2$ was carried out in order to unravel the nature of the coordination sphere about the cerium atom whilst coordinated to the two bulky [Cu(salpn)] ligands. The unsolvated Ln(NO$_3$)$_3$-[Cu(salpn)]$_2$ complexes could not be crystallized. An illustration of the molecule and the atomic numbering scheme used is presented in Fig. 1. The asymmetric unit consists of a molecule of Ce(NO$_3$)$_3$-[Cu(salpn)]$_2$ and two half molecules of nitromethane. One of these forms a bond to Cu(2) and thus links pairs of the complex, related by the twofold axis along the C–NO$_2$ bond, into dimers (Fig. 2).

The two Cu–Ce distances are 3.325(2) and 3.288(2) Å, which make any metal–metal interaction unlikely. The cerium ion is decacoordinate with six O-atoms from three bidentate nitrate groups and four O-atoms from the two [Cu(salpn)] ligands forming an irregular polyhedron. The arrangement of these O-atoms conforms to none of the usual

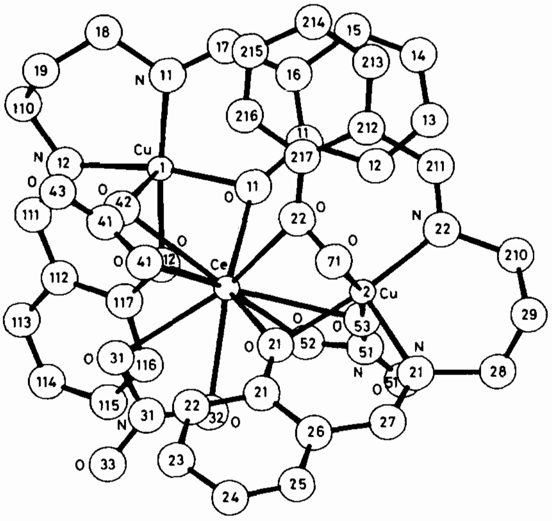

Fig. 1. Drawing of Ce(NO$_3$)$_3$[Cu(salpn)]$_2$ showing the numbering scheme. The carbon atoms are unlabelled.

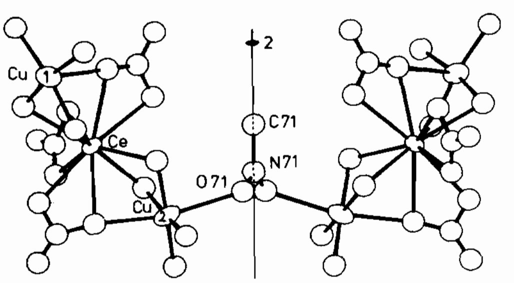

Fig. 2. Pair of Ce(NO$_3$)$_3$[Cu(salpn)]$_2$ complex molecules linked by a bridging nitromethane molecule. The organic ligand is not completely drawn.

polyhedra for decacoordination. The strongly directional bonding about the Cu(II) ions is probably partly responsible for the irregular geometry about the non-directional Ce(III) ion. However, if one considers the overall way that five ligands, *i.e.* two [Cu(salpn)] and three nitrate groups, are packed about the Ce(III) ion, then a more regular geometry is revealed. The coordination sphere may then be said to consist of trigonal bipyramidal arrangement of two axial nitrates (which also bridge to the Cu(II) ions), and one nitrate and the two [Cu(salpn)] ligands in the equatorial plane (Table IV). The two axial distances are significantly longer than the equatorial distances, as usual for such an arrangement; the in-plane angles (total 360°) deviate from the ideal 120° because of the steric crowding by the bulky [Cu(salpn)] ligands: the angle between these latter opens up to 136°. This sort of packing about metal ions has been noted previously for the pentakis(nitrato)europate(III) [13] and for tetrakis-(nitrato)cobaltate(II) anions [14]. The distances about the Ce(III) ion vary from 2.40 to 2.68 Å; the Ce–O(salpn) distances are rather shorter (2.40–2.55, mean 2.45 Å) than the Ce–O(nitrate) (2.43–2.68, mean 2.59 Å). There appear to be no correlation between the Ce–O bond lengths and the shared O(nitrate)–Cu distances, *i.e.* Ce–O(42) < Ce–O(41), but Ce–O(53) > Ce–O(52), although it is O(42) and O(55) which are shared with the Cu(II) ions.

TABLE IV. Bond Lengths (Å) and Angles (°) for the Idealized Trigonal Bipyramidal Arrangement of the Five Ligands about the Ce(III) Ion in $\mathrm{Ce(NO_3)_3[Cu(salpn)]_2}$[a].

Ce–O(1)	2.16	Ce–O(2)	2.02	Ce–O(3)	2.30
Ce–O(4)	2.41			Ce–O(5)	2.42
O(1)–Ce–O(2)	136			O(2)–Ce–O(4)	88
O(1)–Ce–O(3)	110			O(2)–Ce–O(5)	82
O(1)–Ce–O(4)	92			O(3)–Ce–O(4)	91
O(1)–Ce–O(5)	92			O(3)–Ce–O(5)	97
O(2)–Ce–O(3)	114			O(4)–Ce–O(5)	169

[a] O(i), i = 1–4 Is the midpoint of O(i1), O(i2); O(5) is the midpoint of O(52), O(53); i = 1–3 correspond to equatorial ligands and i = 4,5 to the two axial nitrate groups.

The Cu(II) ions, which on the basis of spectroscopic measurements [15] are reported to be *cis*-square planar in the deep violet coloured free ligand, adopt higher coordination in the complex; Cu(1) is pentacoordinate with a fairly regular square-based pyramidal geometry. The in-plane distances are closely similar, 1.93–1.98 Å, but there is a longer axial bond to a shared nitrate O-atom, 2.56 Å. By contrast, Cu(2) succeeds in adopting an elongated octahedral geometry with four similar in-plane bonds to the salpn ligand, 1.93–2.01 Å, and two longer bonds to a shared nitrate O-atom, 2.28 Å and to a nitromethane oxygen, 2.54 Å. This elongated octahedral geometry is not untypical for a Jahn-Teller distorted d^9 configuration.

The three nitrate groups are all distorted from D_{3h} symmetry. The nitrate which is symmetrically bidentate to the Ce(III) ion is the least distorted and approximates to C_{2v} symmetry. The other nitrates are tricoordinate (using only two O-atoms) since they are bridging to the Cu(II) ion and are therefore severely distorted, in particular $\mathrm{N(51)O_3^-}$. The O-atoms of this latter have high thermal parameters indicating some fluxional behaviour. Three peaks in the final Fourier difference map lie in close proximity of these O-atoms and an attempt was made to model two alternative positions, but without success. The bond lengths and angles in the Schiff's base ligand compare well with those of [Cu(salen)] and [Cu(salen)(H_2O)] [16–17]. The presence of the propylene group as opposed to the ethylene in salen, permits greater flexibility, which accounts for the fact that [Cu(salpn)] and not [Cu(salen)] forms complexes with lanthanide nitrates. This greater flexibility is reflected in the angles between the normals to planes of benzene rings, which are 38 and 56° in $\mathrm{Ln(NO_3)_3[Cu(salpn)]_2}$ and only 5° in [Cu(salen)(H_2O)], where the ligand is practically planar. An interesting feature of the structure is the participation of one of the nitromethane molecules in the bonding to a copper atom. Due to spectral interferences, no IR band could be assigned to the NO_2 stretching modes of the nitromethane molecule. This molecule has a significantly longer C–N bond length (1.57 Å) as compared with that of the non-bonding molecule (1.37 Å). However, the N–O distances are little affected on coordination; the removal of electron density from the NO_2 group results in a contraction in the O–N–O angle from 125 to 116° showing a decrease in repulsion between the O-atoms. In nitromethane crystals, this angle is 123° [18]. Nitromethane is only a weak donor towards first row transition metals and whilst solvates are not uncommon, it is often found 'isolated' in the lattice, *e.g.* in [Fe(salen)]·CH_3NO_2 [19]. Crystals of [$CuCl_2$(di-2-pyridylketoxime)]·CH_3NO_2 gradually loose nitromethane at room temperature, suggesting that the solvent molecule is weakly bound, if at all [20]. However, in the crystal structure of $\mathrm{[Cu(NO_3)_2(CH_3NO_2)]}$, the copper is five coordinate with four in-plane O(nitrate)-atoms and a fifth interaction to a nitromethane oxygen (2.31(3) Å) completes a square pyramid about the Cu(II) ion [21].

Apart from this nitromethane bridge between the Cu(2) atoms, there are no significant intermolecular interactions. The other nitromethane molecule makes only one contact <3.00 Å to the H-atom of an azomethine group (O(61)–H(17): 2.51(2) Å). Two of the nitrate O-atoms that are not bonded to Ce or Cu make contacts with azomethine H-atoms (O(43)–H(211) = 2.46(2) Å and O(51)–H(17) = 2.75(2) Å). The overall packing is probably dominated by weak Van der Waals interactions between aligned benzene rings.

The Nickel Complexes

The complex ligand [Ni(salpn)(pn)], but not [Ni(salpn)], gave a series of complexes with $Ln(NO_3)_3$ that analyzed as $Ln(NO_3)_3[Ni(salpn)(pn)]_2 \cdot 2H_2O$, Ln = La–Lu. The X-ray powder photographs of the complexes with Ln = Ce–Lu indicate an isostructural series of compounds. Vibrational and electronic reflectance spectra have been recorded for the nickel complexes and compared with those obtained for the copper series in an attempt to deduce useful structural informations since a structure determination was not possible due to the decomposition of the crystals. The infrared spectra which are identical across the series show that the C–N and C–O stretching frequencies of the salpn ligand are shifted to higher frequencies, from 1628 and 1540 cm^{-1}, respectively, for [Ni(salpn)(pn)] to 1630 and 1555 cm^{-1} in $Ce(NO_3)_3[Ni(salpn)(pn)]_2 \cdot 2H_2O$, compatible with increasing constraint as a result of bridging by the O-atoms; a similar effect was noted for the copper complexes [3]. Bands at 832, 1040, 1285 and 1490 cm^{-1} in the Ni-complexes are assigned to bidentate nitrates and are similar to those reported for the Cu-complexes [3]. The Ni-complexes also exhibit two distinctive bands at 3280 and 3335 cm^{-1} arising from N–H stretch of pn which are at slightly higher frequency than in free [Ni(salpn)(pn)]; this shift is consistent with less electron drain towards the Ni(II) ion from pn, suggesting that either a nitrate group or water molecules are also binding to the nickel. In general, the similarity between the IR spectra of both series of complexes suggests they may have similar structures. The electronic spectra are dominated by d–d transitions and an intense ligand absorption (200–400 nm). In the copper complexes significant changes occur upon complexation to the lanthanide nitrates, due to the distortion of the planar CuO_2N_2 chromophore and the addition of ligand(s). In the case of the Ni-complexes there is a slight change on going from the free ligand to the trinuclear complexes, with the band at *ca.* 550 nm shifted to 570 nm in the complex. The spectra of freshly prepared solutions are similar to the solid state spectra, but the Ni-complexes slowly decompose in solution. The change in colour from yellow brown to bright green of the complexes during the preparation suggests possibly a change from 5-coordinate NiN_3O_2 chromophore to octahedral NiN_3O_3 in the complexes. Attempts were made to prepare complexes containing other transition metals, using [M(salpn)], M = VO, Mn, Co, and Ni. Pure products could not be isolated. The Schiff's base was varied as well and bases obtained from the condensation of salicylaldehyde with 1,2-diaminoethane(salen), 1,2-diaminobenzene(salphen), and from the condensation of 2-hydroxy-acetophenone with 1,3-diaminopropane were studied. Only the latter, which has a methyl substituent on the azomethine carbon forms polynuclear complexes and these are being studied at present.

In conclusion, this work demonstrates the ability of nickel and copper Schiff's base compounds to act as ligands to rare earth cations. The crystal structure determination presented for $Ce(NO_3)_3[Cu(salpn)]_2 \cdot CH_3NO_2$ shows that this is possible by sharing of the phenolate O-atoms, as previously suggested [3]. This type of complexes may prove valuable in the study of 3d–4f metal ion interactions.

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