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The Crystal and Molecular Structure of Tris(antipyrine)trinitratoneodymium, $Nd(NO_3)_3(C_{11}H_{12}ON_2)_3$

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$Nd(NO_3)_3(C_{11}H_{12}ON_2)_3$ is monoclinic, space group $P2_1/c$, with $a=10·887$ (5), $b=16·842$ (9), $c=21·890$ (8) Å, $\beta=107·92$ (3)°, $Z=4$. The structure was solved by the heavy-atom method and refined by least-squares calculations to an R of 0·038 for 4230 counter reflexions. The Nd^{3+} ion is surrounded by nine O atoms forming a tricapped trigonal prism with Nd–O varying between 2·34 and 2·57 Å.

Introduction

The present study forms part of a systematic X-ray investigation of the structures of lanthanide complexes with the object of correlating the effect of the lanthanide contraction with changes in coordination number and crystal structure. The structures of $La(NO_3)_3.4(CH_3)_2SO$ (Krishna Bhandary & Manohar, 1973) and $Yb(NO_3)_3.3(CH_3)_2SO$ (Krishna Bhandary, Manohar & Venkatesan, 1975) have already been established and it has been shown that the coordination of Yb^{3+} is different from that of La^{3+}. In the present structure the dimethyl sulphoxide group is replaced by a bulkier ligand, antipyrine.

Experimental

$Nd(NO_3)_3(C_{11}H_{12}ON_2)_3$ was prepared (Krishna Murthy & Soundararajan, 1967) and recrystallized from methanol. The crystals were tabular, elongated along **c**. They were examined by rotation and Weissenberg techniques; cell dimensions were subsequently refined on the diffractometer by least-squares calculations (Mo $K\alpha$, $\lambda=0·7107$ Å).

Crystal data

$Nd(NO_3)_3(C_{11}H_{12}ON_2)_3$; $M=895$, $a=10·887$ (5), $b=16·842$ (9), $c=21·890$ (8) Å, $\beta=107·92$ (3)°, $V=3818·9$ Å^3. Space group: $P2_1/c$, $D_c=1·556$, $D_m=1·547$ g cm^{-3} (flotation), $Z=4$, $F(000)=1800$, $\mu=14·50$ cm^{-1} (Mo $K\alpha$).

Intensities were collected on a Picker/FACS-I diffractometer by the 2θ scan technique up to $2\theta=45°$ with a crystal, $0·16\times0·32\times(0·48–0·6)$ mm, and graphite-monochromated Mo $K\alpha$ radiation. 5029 reflexions were measured, of which 799 were considered unobserved ($<3\sigma$). They were corrected for Lorentz and polarization effects. Absorption corrections were applied with a modified version of *ORABS* (Schwarzenbach, 1972). The intensities were then placed on an absolute scale by a Wilson (1942) plot.

Structure determination and refinement

The Nd position was deduced from a Patterson map and refined with an isotropic temperature factor of 3·0 Å^2. After three cycles $R\ [=\sum||F_o|-|F_c||/\sum|F_o|]$ was 0·31. The coordinates of the remaining non-hydrogen atoms were obtained from a Fourier map phased on Nd with planes for which $|F_c|\geq 0·6\ |F_o|$. A structure factor calculation with an overall isotropic temperature factor of 3·0 Å^2 gave $R=0·22$.

Table 1. *Final fractional atomic coordinates with e.s.d.'s in parentheses*

	x	y	z
Nd	0·12635 (3)	0·21437 (2)	0·14499 (2)
O(1)	0·18635 (44)	0·13660 (32)	0·25016 (22)
O(2)	0·34070 (41)	0·20415 (30)	0·23422 (23)
O(3)	0·37931 (60)	0·12412 (39)	0·31529 (28)
O(4)	0·24967 (47)	0·34425 (29)	0·14532 (26)
O(5)	0·29074 (45)	0·24885 (27)	0·08886 (24)
O(6)	0·35978 (62)	0·36698 (38)	0·08004 (36)
O(7)	0·22367 (42)	0·08173 (26)	0·13403 (21)
O(8)	0·09622 (46)	0·12558 (28)	0·04597 (22)
O(9)	0·20056 (53)	0·01655 (29)	0·04729 (25)
O(10)	0·04963 (43)	0·29860 (30)	0·21099 (21)
O(11)	0·00073 (40)	0·29009 (29)	0·05875 (21)
O(12)	−0·07092 (40)	0·14938 (30)	0·13233 (22)
N(1)	0·30181 (59)	0·15432 (37)	0·26701 (26)
N(2)	0·30145 (55)	0·32023 (37)	0·10506 (31)
N(3)	0·17259 (51)	0·07443 (31)	0·07423 (26)
N(4)	−0·00329 (50)	0·35958 (34)	0·29265 (24)
N(5)	0·06096 (51)	0·38774 (34)	0·35389 (25)
N(6)	−0·14351 (49)	0·37048 (31)	−0·01352 (25)
N(7)	−0·24795 (51)	0·41825 (33)	−0·01296 (26)
N(8)	−0·28683 (47)	0·12586 (35)	0·11129 (26)

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Table 1 (*cont.*)

N(9)	−0·36594 (54)	0·09340 (36)	0·14359 (30)
C(1)	0·08657 (64)	0·32956 (42)	0·26649 (32)
C(2)	0·20832 (65)	0·34147 (42)	0·31092 (32)
C(3)	0·19025 (66)	0·37843 (42)	0·36517 (35)
C(4)	0·28608 (70)	0·40445 (50)	0·42650 (36)
C(5)	−0·00339 (71)	0·42847 (49)	0·39379 (34)
C(6)	−0·14066 (60)	0·35338 (43)	0·27057 (30)
C(7)	−0·19302 (73)	0·27918 (50)	0·27150 (37)
C(8)	−0·33169 (86)	0·27312 (56)	0·25133 (44)
C(9)	−0·40584 (79)	0·34123 (58)	0·23357 (40)
C(10)	−0·34979 (77)	0·41485 (55)	0·23204 (37)
C(11)	−0·21139 (69)	0·42319 (48)	0·25107 (34)
C(12)	−0·10012 (60)	0·33109 (38)	0·04511 (31)
C(13)	−0·18368 (59)	0·34944 (41)	0·08106 (33)
C(14)	−0·27202 (66)	0·40230 (43)	0·04394 (33)
C(15)	−0·38495 (72)	0·44369 (54)	0·05874 (38)
C(16)	−0·35060 (67)	0·43503 (47)	−0·07542 (34)
C(17)	−0·06910 (62)	0·38901 (42)	−0·05543 (30)
C(18)	0·00451 (71)	0·32558 (48)	−0·06882 (34)
C(19)	0·08352 (79)	0·35479 (57)	−0·10843 (36)
C(20)	0·08307 (84)	0·42490 (56)	−0·13164 (38)
C(21)	0·00540 (78)	0·48249 (51)	−0·11827 (35)
C(22)	−0·07168 (71)	0·46687 (43)	−0·07818 (32)
C(23)	−0·16105 (57)	0·12198 (41)	0·14929 (33)
C(24)	−0·15958 (67)	0·08444 (45)	0·20741 (35)
C(25)	−0·28691 (74)	0·06636 (49)	0·20155 (36)
C(26)	−0·34208 (88)	0·02334 (61)	0·24965 (42)
C(27)	−0·50104 (68)	0·06919 (55)	0·11060 (43)
C(28)	−0·33881 (61)	0·16217 (41)	0·04999 (32)
C(29)	−0·44077 (64)	0·21764 (46)	0·03982 (38)
C(30)	−0·48996 (79)	0·25069 (45)	−0·02188 (43)
C(31)	−0·43679 (82)	0·22926 (49)	−0·06995 (41)
C(32)	−0·33256 (79)	0·17456 (49)	−0·05832 (38)
C(33)	−0·28321 (68)	0·14057 (42)	0·00257 (33)

For refinement the structure was split into two groups, one containging two antipyrine groups and Nd^{3+}, the other one antipyrine and three nitrate groups. R converged to 0·084 with isotropic temperature factors for all atoms. The function minimized in the least-squares program (Shiono, 1972), adapted to the IBM 360/44 computer by B. S. Reddy, was $\sum W(|F_o|-|F_c|)^2$. The weighting function (Cruickshank, Bujosa, Lovell & Truter, 1961) was $W=1/(a+|F_o|+c|F_o|^2)$, with $a=16{\cdot}0$ and $c=0{\cdot}0045$. Scattering factors were from Cromer & Waber (1965).

At this stage, the reflexions were given individual weights based on counting statistics and the scattering factor of Nd^{3+} was corrected for anomalous dispersion ($\Delta f'=0{\cdot}39$ and $\Delta f''=-3{\cdot}41$). Anisotropic temperature factors were introduced for all atoms. Refinement reduced R to 0·040. The concluding cycles were done on the CDC 6400/6600 computer at the ETH, Zürich, with *CRYLSQ* of the X-RAY System (1972). All parameters were refined together by block-diagonal least-squares calculations. In the final cycle, the shifts in the positional parameters were about one hundredth the standard deviations and the final R for the observed reflexions was 0·038. A difference map failed to show peaks which could be assigned unambiguously to H atoms.

The final coordinates of all non-hydrogen atoms are given in Table 1 and the thermal parameters in Table 2. Bond lengths and angles are listed in Table 3. The aver-

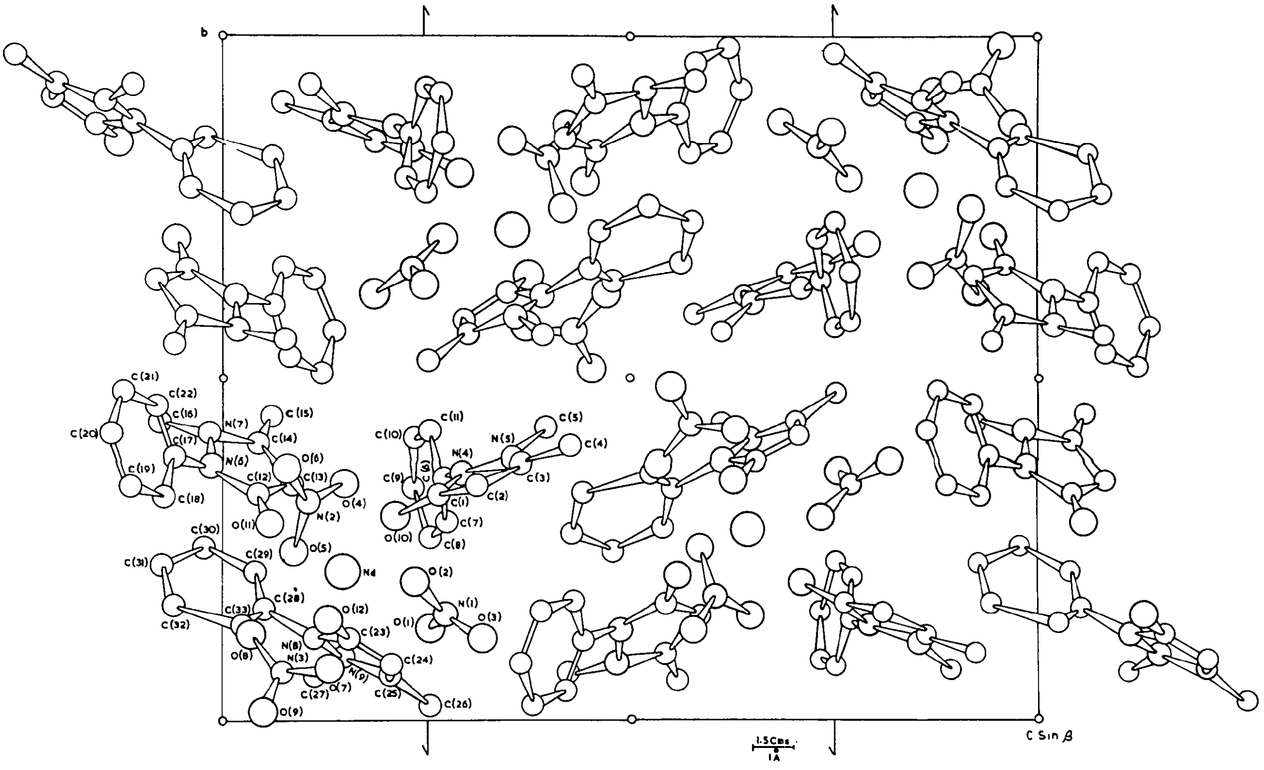

Fig. 1. Structure viewed down a.

age standard deviations in the lengths of Nd–O, N–O, N–N, C–N, C–O and C–C are 0·005, 0·008, 0·008, 0·009, 0·008 and 0·012 Å respectively.*

Description and discussion of the structure

(*a*) *Crystal packing*

The structure viewed down **a** is shown in Fig. 1. The Nd^{3+} ion is surrounded by nine O atoms, three from the three antipyrine and six from the three nitrate groups. All three nitrate groups are bidentate in contradiction to the earlier suggestion from physico-

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* A table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31325 (6 pp.). Copies may be obtained from The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Anisotropic thermal parameters* (× 10^4).

The temperature factor is $\exp[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2klb^*c^*U_{23}+2hla^*c^*U_{13}+2hka^*b^*U_{12})]$. Standard deviations are given in parentheses.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Nd	306 (2)	456 (2)	405 (2)	37 (2)	148 (2)	−15 (3)
O(1)	610 (33)	1166 (47)	611 (34)	−33 (34)	166 (28)	176 (33)
O(2)	492 (29)	829 (39)	857 (38)	−55 (31)	30 (27)	22 (34)
O(3)	1195 (53)	1360 (61)	933 (48)	243 (48)	−189 (42)	252 (44)
O(4)	726 (36)	618 (37)	1164 (46)	−57 (31)	361 (35)	−133 (35)
O(5)	761 (35)	584 (34)	1095 (43)	5 (28)	600 (34)	61 (31)
O(6)	1309 (58)	1144 (55)	2120 (76)	−305 (47)	955 (57)	388 (54)
O(7)	688 (33)	555 (32)	623 (33)	153 (27)	244 (27)	50 (27)
O(8)	808 (36)	667 (37)	600 (33)	205 (31)	138 (29)	−59 (28)
O(9)	1170 (46)	638 (38)	956 (43)	2 (35)	553 (38)	−235 (33)
O(10)	696 (33)	973 (43)	593 (32)	222 (33)	246 (27)	−215 (31)
O(11)	578 (29)	688 (34)	683 (32)	172 (31)	176 (26)	183 (31)
O(12)	397 (28)	896 (40)	783 (36)	−116 (29)	184 (27)	−37 (32)
N(1)	812 (48)	853 (51)	526 (39)	140 (43)	57 (36)	−17 (38)
N(2)	574 (42)	739 (51)	1101 (55)	−71 (37)	315 (41)	201 (42)
N(3)	651 (40)	500 (38)	623 (41)	−104 (32)	347 (34)	−113 (33)
N(4)	573 (38)	732 (44)	468 (36)	134 (35)	199 (31)	−169 (34)
N(5)	607 (39)	718 (45)	525 (38)	142 (35)	154 (32)	−143 (34)
N(6)	521 (36)	513 (39)	561 (38)	103 (31)	153 (31)	80 (32)
N(7)	607 (39)	590 (42)	709 (42)	188 (34)	282 (34)	97 (35)
N(8)	404 (34)	744 (47)	708 (42)	−122 (33)	289 (32)	−13 (36)
N(9)	579 (38)	952 (50)	843 (45)	−100 (41)	370 (35)	−51 (45)
C(1)	614 (49)	646 (53)	553 (48)	170 (42)	262 (41)	−62 (42)
C(2)	570 (48)	607 (53)	608 (50)	117 (43)	154 (41)	−107 (43)
C(3)	605 (50)	571 (54)	813 (57)	149 (43)	270 (45)	−19 (45)
C(4)	590 (53)	1116 (73)	687 (57)	80 (53)	−117 (46)	−416 (54)
C(5)	765 (58)	1168 (73)	606 (54)	317 (54)	255 (47)	−392 (52)
C(6)	470 (44)	804 (56)	428 (44)	101 (42)	171 (37)	−131 (42)
C(7)	819 (57)	837 (63)	866 (61)	−205 (56)	288 (50)	−169 (57)
C(8)	1007 (73)	1232 (85)	1160 (76)	−232 (69)	430 (63)	−349 (69)
C(9)	839 (63)	1488 (91)	887 (63)	85 (65)	275 (54)	−267 (64)
C(10)	866 (64)	1349 (84)	737 (59)	354 (62)	308 (52)	−17 (59)
C(11)	668 (53)	1016 (67)	584 (52)	340 (50)	269 (44)	16 (49)
C(12)	465 (44)	439 (46)	588 (47)	53 (38)	87 (38)	101 (38)
C(13)	421 (42)	529 (49)	667 (51)	89 (38)	151 (39)	52 (42)
C(14)	563 (49)	736 (56)	607 (51)	−29 (45)	197 (42)	27 (44)
C(15)	691 (56)	1326 (82)	863 (64)	535 (57)	430 (51)	192 (60)
C(16)	577 (51)	937 (65)	534 (50)	265 (49)	−107 (42)	272 (47)
C(17)	517 (45)	762 (56)	385 (42)	−42 (41)	138 (37)	−45 (40)
C(18)	718 (56)	1099 (71)	582 (52)	101 (52)	216 (46)	−253 (50)
C(19)	858 (64)	1472 (86)	628 (58)	−24 (65)	225 (51)	−361 (61)
C(20)	1048 (71)	1382 (87)	669 (60)	−265 (67)	318 (55)	−169 (60)
C(21)	985 (67)	1024 (72)	629 (56)	−359 (58)	269 (52)	−188 (52)
C(22)	862 (58)	693 (56)	436 (46)	−253 (48)	201 (44)	34 (42)
C(23)	300 (39)	636 (55)	743 (53)	−61 (38)	188 (38)	−47 (44)
C(24)	617 (50)	785 (59)	731 (56)	−141 (46)	358 (45)	−100 (48)
C(25)	841 (61)	909(66)	738 (60)	−46 (53)	368 (52)	−110 (51)
C(26)	1198 (80)	1555 (97)	940 (70)	−300 (74)	692 (64)	241 (68)
C(27)	358 (49)	1513 (89)	1352 (83)	−362 (56)	214 (53)	42 (70)
C(28)	461 (45)	557 (51)	630 (50)	−134 (40)	105 (40)	−17 (42)
C(29)	493 (46)	605 (53)	1190 (69)	2 (49)	112 (47)	−164 (57)
C(30)	726 (59)	659 (59)	1198 (78)	−18 (49)	−61 (57)	21 (55)
C(31)	927 (65)	805 (70)	1046 (70)	−192 (58)	−79 (57)	64 (58)
C(32)	903 (66)	858 (67)	779 (62)	−192 (55)	98 (54)	103 (52)
C(33)	720 (53)	604 (54)	668 (54)	−164 (52)	272 (46)	−89 (45)

chemical studies (Krishna Murthy & Soundararajan, 1967) that only one nitrate is likely to be bidentate. Intermolecular contact distances are normal.

(*b*) *Coordination polyhedron*

The Nd–O distances (Table 4) vary between 2·339 (4) and 2·570 (5) Å and agree well with those found in other Nd complexes (Hansson, 1970; Oskarsson, 1971). The average Nd–O(antipyrine) and Nd–O(nitrate) distances are 2·348 (5) and 2·547 (5) Å respectively and the difference is significant.

The coordination polyhedron formed by the nine O atoms around Nd^{3+} is shown in Fig. 2. The two possible ground-state geometries for nine-coordination are the symmetrically tricapped trigonal prism of $\bar{6}m$ (D_{3h}) symmetry and the monocapped square antiprism of $4mm$ (C_{4v}) symmetry. The polyhedron in the present case can be better described as a tricapped trigonal prism. The antipyrine O(10), O(11) and O(12) [plane (1)] form one of the triangular faces of the trigonal prism and the nitrate O(2), O(5) and O(7) [plane (2)] form the other. The nitrate O(1), O(4) and O(8) [plane (3)] are at the centres of the rectangular faces of the trigonal prism. The distances and angles in the coordination polyhedron are given in Table 5 from which it can be seen that the triangles are approximately equilateral. They are slightly inclined with respect to each other, the angles between them being 7° 10′ between planes (1) and (2), 2° 48′ between (2) and (3) and 5° 42′ between (1) and (3). All O···O contacts in the coordination polyhedron are normal, the three closest, O(4)–O(11), O(7)–O(1) and O(8)–O(5), being 2·934, 2·849 and 2·907 Å respectively.

Table 3. *Bond distances* (Å) *and angles* (°) *with their estimated standard deviations*

(*a*) Nitrate groups

N(1)–O(1)	1·233 (8)	O(1)–N(1)–O(2)	118·8 (5)
N(1)–O(2)	1·259 (9)	O(1)–N(1)–O(3)	121·3 (7)
N(1)–O(3)	1·241 (8)	O(2)–N(1)–O(3)	119·9 (6)
N(2)–O(4)	1·251 (9)	O(4)–N(2)–O(5)	119·3 (6)
N(2)–O(5)	1·249 (8)	O(4)–N(2)–O(6)	120·6 (7)
N(2)–O(6)	1·240 (10)	O(5)–N(2)–O(6)	120·1 (7)
N(3)–O(7)	1·261 (7)	O(7)–N(3)–O(8)	118·0 (5)
N(3)–O(8)	1·225 (7)	O(7)–N(3)–O(9)	118·8 (5)
N(3)–O(9)	1·225 (8)	O(9)–N(3)–O(9)	123·2 (5)

(*b*) Antipyrine molecules

Antipyrine (I)

O(10)–C(1)	1·269 (8)	N(4)—C(6)	1·427 (8)
C(1)—C(2)	1·396 (9)	C(6)—C(7)	1·376 (11)
C(1)—N(4)	1·373 (10)	C(7)—C(8)	1·440 (12)
C(2)—C(3)	1·407 (11)	C(8)—C(9)	1·388 (13)
C(3)—C(4)	1·490 (9)	C(9)—C(10)	1·387 (13)
C(3)—N(5)	1·361 (9)	C(10)–C(11)	1·441 (11)
N(5)—C(5)	1·449 (11)	C(11)–C(6)	1·398 (10)
N(5)—N(4)	1·391 (7)		
O(10)–C(1)–C(2)	132·8 (7)	N(5)—N(4)—C(1)	108·4 (5)
O(10)–C(1)–N(4)	119·6 (6)	C(1)—N(4)—C(6)	126·7 (5)
N(4)—C(1)–C(2)	107·6 (6)	N(5)—N(4)—C(6)	121·0 (6)
C(1)—C(2)–C(3)	107·6 (7)	N(4)—C(6)—C(7)	117·2 (6)
C(2)—C(3)–C(4)	130·5 (7)	N(4)—C(6)—C(11)	117·6 (6)
C(2)—C(3)–N(5)	107·6 (6)	C(11)–C(6)—C(7)	125·2 (6)
C(4)—C(3)–N(5)	121·9 (7)	C(6)—C(7)—C(8)	117·4 (7)
C(3)—N(5)–C(5)	127·6 (5)	C(7)—C(8)—C(9)	119·5 (8)
C(3)—N(5)–N(4)	108·7 (6)	C(8)—C(9)—C(10)	121·6 (8)
C(5)—N(5)–N(4)	123·3 (5)	C(9)—C(10)–C(11)	120·6 (8)
		C(10)–C(11)–C(6)	115·8 (7)

Antipyrine (II)

O(11)–C(12)	1·253 (8)	N(6)—C(17)	1·433 (10)
C(12)–C(13)	1·408 (11)	C(17)–C(18)	1·417 (11)
C(12)–N(6)	1·392 (8)	C(18)–C(19)	1·441 (13)
C(13)–C(14)	1·377 (9)	C(19)–C(20)	1·425 (13)
C(14)–C(15)	1·532 (12)	C(20)–C(21)	1·376 (13)
C(14)–N(7)	1·376 (10)	C(21)–C(22)	1·413 (12)
N(7)—C(16)	1·503 (8)	C(22)–C(17)	1·400 (10)
N(7)—N(6)	1·396 (8)		
O(11)–C(12)–C(13)	131·1 (6)	C(13)–C(14)–C(15)	129·0 (7)
O(11)–C(12)–N(6)	120·4 (7)	C(13)–C(14)–N(7)	111·6 (7)
N(6)—C(12)–C(13)	108·5 (5)	C(15)–C(14)–N(7)	119·4 (6)
C(12)–C(13)–C(14)	105·4 (6)	C(14)–N(7)—C(16)	124·4 (6)
C(14)–N(7)—N(6)	106·1 (5)	C(22)–C(17)–C(18)	125·7 (7)
C(16)–N(7)—N(6)	118·7 (6)	C(17)–C(18)–C(19)	115·2 (7)
N(7)—N(6)—C(12)	108·2 (6)	C(18)–C(19)–C(20)	119·9 (8)
C(12)–N(6)—C(17)	126·6 (5)	C(19)–C(20)–C(21)	121·2 (9)
N(7)—N(6)—C(17)	120·2 (5)	C(20)–C(21)–C(22)	121·5 (8)
N(6)—C(17)–C(22)	118·6 (6)	C(21)–C(22)–C(17)	116·4 (7)
N(6)—C(17)–C(18)	115·7 (6)		

Table 3 (*cont.*)

Antipyrine (III)

O(12)–C(23)	1·240 (9)	N(9)—N(8)	1·384 (9)
C(23)–N(8)	1·368 (7)	N(8)—C(28)	1·424 (8)
C(23)–C(24)	1·416 (11)	C(28)–C(29)	1·415 (10)
C(24)–C(25)	1·386 (11)	C(29)–C(30)	1·406 (12)
C(25)–C(26)	1·544 (14)	C(30)–C(31)	1·396 (14)
C(25)–N(9)	1·373 (9)	C(31)–C(32)	1·422 (12)
N(9)—C(27)	1·482 (9)	C(32)–C(33)	1·397 (10)
		C(33)–C(28)	1·401 (11)
O(12)–C(23)–N(8)	122·4 (6)	N(9)—N(8)—C(23)	109·5 (5)
O(12)–C(23)–C(24)	130·1 (6)	N(9)—N(8)—C(28)	121·5 (5)
N(8)—C(23)–C(24)	107·5 (6)	C(23)–N(8)—C(28)	128·8 (6)
C(23)–C(24)–C(25)	106·3 (6)	N(8)—C(28)–C(33)	116·7 (6)
C(24)–C(25)–C(26)	128·9 (7)	N(8)—C(28)–C(29)	119·8 (7)
C(24)–C(25)–N(9)	109·7 (7)	C(33)–C(28)–C(29)	123·5 (7)
C(26)–C(25)–N(9)	121·4 (7)	C(28)–C(29)–C(30)	117·5 (8)
C(25)–N(9)—C(27)	127·2 (7)	C(29)–C(30)–C(31)	119·9 (7)
C(25)–N(9)—N(8)	107·0 (6)	C(30)–C(31)–C(32)	121·7 (8)
C(27)–N(9)—N(8)	122·7 (6)	C(31)–C(32)–C(33)	119·2 (8)
		C(32)–C(33)–C(28)	118·3 (7)

Table 4. *Metal–oxygen coordinating distances* (Å)

Nd–O(1)	2·553 (5)	Nd–O(8)	2·570 (5)
Nd–O(2)	2·547 (4)	Nd–O(10)	2·354 (5)
Nd–O(4)	2·565 (5)	Nd–O(11)	2·339 (4)
Nd–O(5)	2·530 (6)	Nd–O(12)	2·350 (5)
Nd–O(7)	2·515 (5)		

Table 5. *Distances* (Å) *and angles* (°) *in the coordination polyhedron*

O(2)—O(5)	3·150	O(2)—O(5)—O(7)	56·8
O(2)—O(7)	2·994	O(5)—O(7)—O(2)	61·7
O(5)—O(7)	3·143	O(7)—O(2)—O(5)	61·5
O(10)–O(11)	3·212	O(10)–O(11)–O(12)	58·8
O(10)–O(12)	3·101	O(11)–O(12)–O(10)	62·4
O(11)–O(12)	3·097	O(12)–O(10)–O(11)	58·7
O(1)—O(4)	4·353	O(1)—O(4)—O(8)	58·9
O(1)—O(8)	4·275	O(4)—O(8)—O(1)	60·7
O(4)—O(8)	4·342	O(8)—O(1)—O(4)	60·4
O(2)—O(10)	3·441		
O(5)—O(11)	3·099		
O(7)—O(12)	3·393		

(*c*) *Nitrate groups*

The average N–O length [1·246 (8) Å] involving the coordinated O atoms is slightly longer than that [1·236 (8) Å] involving the non-coordinated O though the difference is not significant. Further, the average O–N–O angle involving the coordinated O atoms is 118·7 (5)° whereas the average of the other two is 120·7 (6)°. These results are consistent with observations made by Addison, Logan, Wallwork & Garner (1971).

(*d*) *Antipyrine molecules*

The mean values of chemically equivalent bond lengths and angles in the three independent antipyrine groups are given in Fig. 3. The mean bond lengths and angles of the phenyl rings vary between 1·385 and 1·429 Å and 116·7 and 124·8° and are normal. The average N–C distance of 1·428 Å between the phenyl and pyrazolone rings is close to the expected 1·44 Å for a C(sp^2)–N(sp^2) bond (Dewar & Schmeising, 1959) suggesting that there is no appreciable delocalization of π electrons between the two rings. On the other hand, the bond lengths in the pyrazolone ring suggest delocalization of π electrons within the ring. The C–C(Me) and N–C(Me) bonds vary from 1·490 (9) to 1·544 (14) Å and 1·449 (11) to 1·503 (8) Å respectively. The mean distances of 1·522 and 1·478 Å are not significantly different from the values of 1·50 Å (Sundaralingam & Putkey, 1970) and 1·47 Å (*International Tables for X-ray Crystallography*, 1962) expected for C(sp^2)–C(sp^3) and N(sp^2)–C(sp^3) bonds respectively.

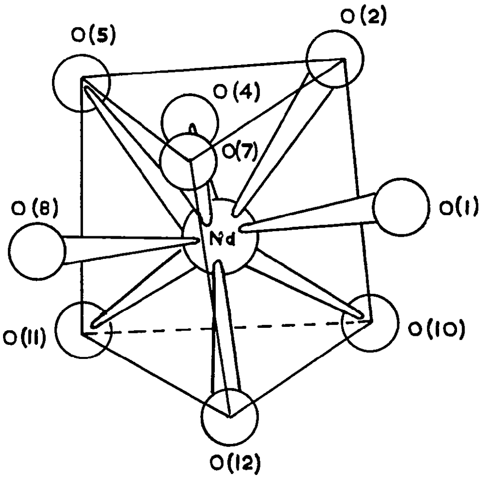


Fig. 2. Coordination polyhedron around Nd^{3+}.

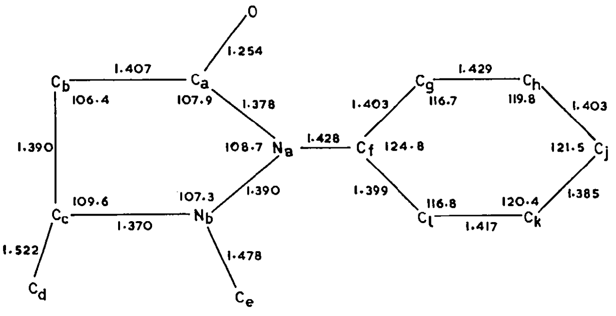


Fig. 3. Mean values of chemically equivalent bond lengths and angles of the antipyrine ligands.

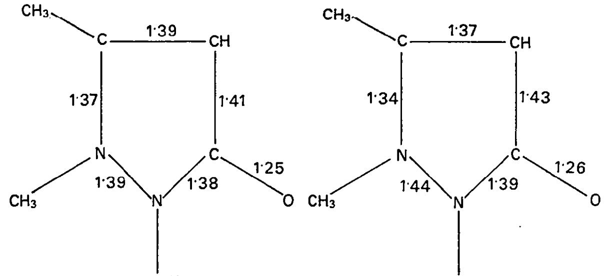
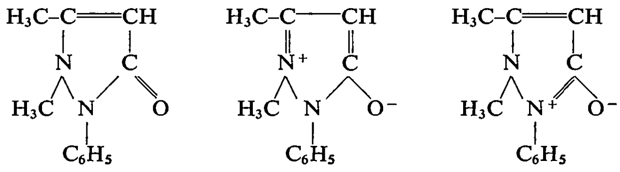


Fig. 4. (*a*) Observed and (*b*) calculated bond lengths (Å) in the pyrazolone moiety.

The structure of the antipyrine molecule can be considered as a mixture of a number of resonating structures. The three important canonical structures (Knorr, 1887; Michaelis, 1902; Kitamura, 1940) are:



(I) (II) (III)

The relative contributions of the valence structures in the present study have been calculated to be 55 %, 30 % and 15 % respectively. The observed bond lengths and the values calculated on the basis of these contributions are shown in Fig. 4. Pauling's (1960) semi-empirical formula

$$D_n = D_1 - (D_1 - D_2)\ 1{\cdot}84(n-1)/(0{\cdot}84n + 0{\cdot}16)\,,$$

where D_n is the value of the interatomic distance of intermediate type, D_1 that for a single bond, D_2 that for a double bond, and n the bond number, was used to calculate the C–C distance. The C–N distances were obtained from

$$r_x = r_1 - (r_1 - r_2)\ 3x/(2x+1)$$

(Donohue, Lavine & Rollett, 1956), where r_1 and r_2 correspond to the single and double bond distances respectively and x is the bond order. The C–O distances were taken from the curve given by Curl (1959). The contributions of the three canonical forms in the free antipyrine molecule (Singh & Vijayan, 1973) are 66 %, 22 % and 12 % respectively. As expected the contribution of form (I) is less in the present case than in free antipyrine. This is reflected in the average C–O length, 1·254 (8) Å in the present case, compared to 1·237 Å in free antipyrine. Thus the contributions of (II) and (III) containing polarized O atoms are enhanced on association of antipyrine with metal ions.

The rings of the antipyrine molecules are essentially planar. However, in all three independent antipyrine molecules the methyl C_e (Fig. 3) and the O atom deviate quite considerably from the plane through the pyrazolone ring. The amount of deviation appears to be related to the torsion angle between the phenyl and pyrazolone rings. In antipyrine (I), the angle between the two planar parts of the molecule is the largest (73·1°) and correspondingly the deviation of C_e is least (0·093 Å). On the other hand, in antipyrine (II) the angle between the rings is least (37·8°) while the deviation of C_e is largest (0·655 Å). In antipyrine (III), the corresponding values are 49°49′ and 0·346 Å respectively. Again for the O atom the deviation is largest (0·116 Å) in antipyrine (II), whereas it is smaller and approximately the same (0·026 Å) in the other two rings. It is therefore apparent that steric factors are responsible for this situation. The smaller deviation of the O atom compared to that of C_e is due to its association with the metal ion.

A feature of the structure is that, even though the five-membered ring is essentially planar, N_a and N_b tend to show slightly larger deviations than the C atoms. The deviations of the N atoms from the planes through the three surrounding atoms are given in Table 6: they suggest a slight pyramidal character for the N atoms. This has also been observed in free antipyrine (Singh & Vijayan, 1973) and is reminiscent of the situation found in the amide linkage in peptides, where the N atom is significantly out of the plane through the three surrounding atoms (Winkler & Dunitz, 1971; Vasantha Pattabhi, Venkatesan & Hall 1974).

Table 6. *Displacements* (Å) *of nitrogen atoms from the planes of their nearest neighbours in antipyrine*

(i) Plane through C_a, C_f, N_b

	Antipyrine (I)	Antipyrine (II)	Antipyrine (III)
N_a	0·0746	−0·1820	−0·0347
	Equation to the plane is $AX+BY+CZ=D$		
A	0·12964	0·37854	0·21623
B	0·89757	0·75516	0·88103
C	−0·42137	0·53520	0·42008
D	2·53266	4·18622	3·71479

(ii) Plane through C_c, C_e, N_a

	Antipyrine (I)	Antipyrine (II)	Antipyrine (III)
N_b	−0·0507	0·2713	0·1449
	Equation to the plane is $AX+BY+CZ=D$		
A	0·21555	0·39720	−0·35775
B	0·88316	0·89769	0·86718
C	−0·41662	0·19077	0·34642
D	2·37647	4·96308	4·02644

The phenyl rings are rotated by 73°7′, 37°49′ and and 49°49′ with respect to the pyrazolone ring in the three antipyrine groups. The torsion angles are observed to have different values in antipyrine and in other complexes of antipyrine (Singh & Vijayan, 1973; Vijayan & Viswamitra, 1968; Cingi, Guastini, Musatti & Nardelli, 1972; Brassy, Mornon & Delettré, 1974; Brassy, Renaud, Delettré & Mornon, 1974). The widely varying angles of rotation between the rings suggest that intermolecular forces play an important role in the conformation of the molecule.

Another point of note is the interaction between the pyrazolone ring of antipyrine (II) and the phenyl ring of antipyrine (III). The overlap of the rings seen down **c** is shown in Fig. 5. The distance between the centre of gravity of the planes through the rings is about 3·5 Å and the angle between the two planes is 10·5°.

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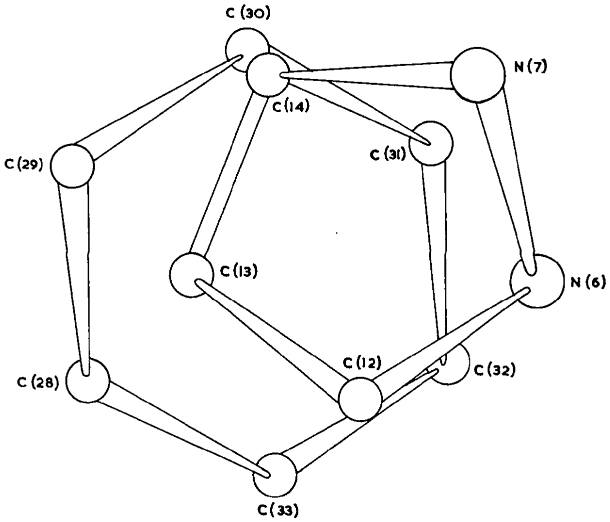

Fig. 5. Overlap of the pyrazolone and phenyl rings viewed down **c**.

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The Crystal and Molecular Structure of a New Type of Paramagnetic Binuclear Rhenium(IV) Compound, $Cs_3Re_2OCl_{10}$

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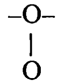
The crystal and molecular structure of $Cs_3Re_2OCl_{10}$ has been determined by single-crystal diffractometry. All atoms conform to the space group $I4/mmm$ with $a = 7{\cdot}393$ (3), $c = 17{\cdot}51$ (2) Å; $Z = 2$. The intensities of 558 reflexions were collected on a $P2_1$ Syntex four-circle diffractometer with a graphite monochromator using Mo $K\alpha$ radiation and the 2θ–ω scan technique. The structure was solved by the heavy-atom method and refined by block-diagonal least squares. The final $R = 0{\cdot}035$, $R_w = 0{\cdot}033$ for 371 non-zero reflexions. The molecular anion has a linear arrangement of the Cl–Re–O–Re–Cl group, Re–O = 1·832 (3) Å. The bridging O atom is formally occupied by one unpaired electron and that is the reason for the paramagnetism of the compound.

Introduction

The binuclear rhenium(IV) complex of the $K_4Re_2OCl_{10}$ type was prepared for the first time by Jeżowska-Trzebiatowska (1939). Morrow (1962) suggested that this compound crystallizes as a salt like $K_4Re_2OCl_{10}.H_2O$ Our crystallographic studies (Lis, Głowiak and Jeżowska-Trzebiatowska, 1975) have shown that this compound forms non-hydrated crystals. This complex forms a blood-red compound in a dilute hydrochloric acid solution when oxidizing agents are added. The effect of the addition of oxidizers to μ-oxochlororhenate was discovered by Jeżowska-Trzebiatowska (1951), Jeżowska-Trzebiatowska & Przywarska (1955, 1958*a*, *b*, 1961) and Jeżowska-Trzebiatowska, Mroziński & Wojciechowski (1969). On the basis of more experimental results it was suggested that the blood-red compound has the formula $Cs_3Re_2O_2HCl_{10}$, and that the  $-\underset{\underset{\displaystyle O}{|}}{O}-$ or –O–O– group forms a bridge between two rhenium(IV) atoms. Hence the determination of the detailed crystal structure of this compound was of considerable interest. We obtained crystals of the blood-red compound for the caesium, potassium and quinoline salts. In this paper are given the results of investigations on the crystal structure of the caesium salt.

Experimental

The investigated compound was prepared by applying a modification of the method given by Jeżowska-Trzebiatowska, Mroziński & Wojciechowski (1969). Hydrogen peroxide was added to the μ-oxochlororhenate in $3M$ hydrochloric acid solution until the solution turned blood-red. The blood-red solution was