Alkali-metal Complexes. Part VII.† Crystal and Molecular Structures of the *o*-Nitrophenolatobis(1,10-phenanthroline) Complexes of Sodium and Rubidium

By **David L. Hughes,*** A.R.C. Unit of Structural Chemistry, Inveresk House, 346 Strand, London WC2R 0HG

The structures of the title complexes have been determined by *X*-ray analysis from diffractometer data. The sodium complex has triclinic crystals, a = 10·436(6), b = 10·062(6), c = 14·867(7) Å, α = 96·98(2), β = 104·02(1), γ = 119·12(4)°, and its structure was determined by direct methods. The rubidium complex, isostructural with the corresponding potassium and caesium complexes, is also triclinic, a = 11·413(6), b = 13·214(6), c = 10·068(15) Å, α = 99·06(5), β = 114·80(5), γ = 101·78(3)°; this structure was determined from Patterson and electron-density maps. The structures were refined by least-squares methods to R 0·074 (Na complex, 1371 observed reflections) and 0·051 (Rb complex, 2107 observed reflections).

In the sodium complex, the cation is six-co-ordinate, interacting with the three chelating ligands in pseudo 32 symmetry, and the crystal structure of this complex is of monomeric units. The rubidium complex has a similar pseudo-three-fold symmetry of the chelating ligands but, with a larger co-ordination sphere, the cation also accepts co-ordination with a second *o*-nitrophenolate ion, which thus bridges cations about a centre of symmetry. Dimeric units, bound by van der Waals' forces, form the crystal structure. The packing arrangements in both complexes appear to depend on the interactions of overlapping phenanthroline molecules about centres of symmetry.

The phenanthroline molecules in both complexes have similar dimensions: all are non-planar, but there is no characteristic pattern of bending or twisting. The cations are displaced from the mean planes of the phenanthroline molecules by up to 0·63 Å. In the *o*-nitrophenolate ions, the variations in bond lengths and angles in the ions are significant and are explained in terms of resonance structure and second-order hybridisation effects. The nitro-groups are rotated about the C–N bonds by 18·6 (Na) and 14·5° (Rb).

THE *o*-nitrophenolatobis-(1,10-phenanthroline) alkali-metal complexes are the principal products when large excesses of 1,10-phenanthroline are added to the reaction solutions of the alkali-metal *o*-nitrophenolate in ethanol.[1] They form a series of brightly coloured crystalline compounds, from the orange sodium complex to the deep-red caesium complex.

Preliminary *X*-ray photographic investigations showed that the potassium, rubidium, and caesium complexes are isostructural and that the sodium complex, although different, showed similarities with the others in the diffraction patterns in certain nets of the lattice.

The crystal structure analyses of the sodium and rubidium complexes were undertaken to investigate further the nature of co-ordination in alkali-metal complexes and, in particular, to determine how the co-ordination pattern in the sodium complex differs from that in the others of the series.

EXPERIMENTAL

The cell parameters, determined from Guinier powder *X*-ray photographs, of four *o*-nitrophenolato-bis(1,10-phenanthroline) complexes of alkali metals are recorded in Table 1.

TABLE 1

Cell dimensions, from Guinier powder photographs, of *o*-nitrophenolato-bis(1,10-phenanthroline) complexes of alkali metals

	Cs	Rb	K	Na
a/Å	11·727(3)	11·422(4)	11·085(4)	10·446(4)
b/Å	12·973(4)	13·223(5)	13·488(5)	10·088(3)
c/Å	10·165(3)	10·055(4)	9·997(4)	14·872(5)
α/deg.	99·30(3)	99·11(3)	98·88(4)	96·92(3)
β/deg.	115·20(2)	114·84(3)	114·73(3)	104·04(3)
γ/deg.	101·23(3)	101·70([illegible])	101·52(3)	119·23(3)
U/Å^3	1319·4(6)	1297·9(8)	1281·8(8)	1272·8(7)

o-*Nitrophenolatobis*-(1,10-*phenanthroline*)*sodium*

A small crystal was mounted on a fibre; the edges of the diamond-shaped plate did not coincide with the chosen primitive cell. Preliminary data were recorded on Weissenberg and precession cameras. Cell parameters were determined more accurately, by least-squares refinement, from χ, ϕ, and 2θ settings of 15 reflections measured on a diffractometer, with Mo-K_{α_1} (λ = 0·70926 Å) radiation.

Crystal Data.—$C_{30}H_{20}N_5NaO_3$, M = 521·52, Triclinic, a = 10·436(6), b = 10·062(6), c = 14·867(7) Å, α = 96·98(2), β = 104·02(1), γ = 119·12(4)°, U = 1269·2 Å^3, D_m = 1·37 (flotation in aqueous KI), Z = 2, D_c = 1·364, $F(000)$ = 540. μ(Mo-$K_{\bar{\alpha}}$) = 1·1 cm^{-1}, λ(Mo-$K_{\bar{\alpha}}$) = 0·71069 Å. Space group $P\bar{1}$.

The intensities of 2365 reflections, with $2\theta \leqslant 40°$ were measured on a Picker four-circle automatic diffractometer with scintillation counter, Mo-$K_{\bar{\alpha}}$ radiation (Zr-filter and pulse-height analyser) and a θ—2θ scan. Of these reflections, 1371 were considered observed, the remainder (42%) unobserved, having $I/\sigma_I < 2·0$, where $\sigma_I^2 = T + (b_1 + b_2) \cdot (t_s/50)^2$, where b_1, b_2 are background counts each for 25 s, t_s is time of scan, and T is scan count.

Lorentz and polarisation factors were applied; no absorption corrections were made. Structure amplitudes were then computed.

Structure Analysis.—The structure of the sodium complex was determined by direct methods using adaptations of Hall and Ahmed's SAP series of programs.[2] The preliminary normalisation of the structure factors (by the K curve method [3]) and calculation of the E statistics (which indicated

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* *Present address:* Molecular Structures Department, Rothamsted Experimental Station, Harpenden, Herts. AL5 2JQ.

† Part VI, ref. 14.

[1] A. J. Layton, R. S. Nyholm, A. K. Banerjee, D. E. Fenton, C. N. Lestas, and M. R. Truter, *J. Chem. Soc.* (*A*), 1970, 1894.

[2] S. R. Hall and F. R. Ahmed, Program NRC 4 of, 'NRC Crystallographic Programs for the IBM 360 System.'

[3] After J. and I. L. Karle in 'Computing Methods in Crystallography,' ed. J. S. Rollett, Pergamon Press, Oxford, 1965, chap. 17.

the space group to be $P\bar{1}$) were computed in ECALC; the $\Sigma 2$ related reflection triplets were found in SAP3; SAP4A was modified for use as a multisolution method of sign-determination (particularly for the $P\bar{1}$ case), and starting with seven signed reflections:

$$\left.\begin{array}{ccc}2 & \bar{1} & \bar{3}\\ 1 & \bar{1} & 13\\ 3 & \bar{1} & 10\end{array}\right\}\text{Origin-determining}$$

$$\left.\begin{array}{ccc}0 & \bar{4} & 2\\ 0 & 2 & 0\\ 0 & 7 & 1\\ 5 & \bar{2} & \bar{6}\end{array}\right\}\begin{array}{l}\text{Signs systematically varied to}\\ \text{give 16 sets of signed } E \text{ values.}\end{array}$$

the signs of 154 reflections with $|E| > 1{\cdot}80$ were determined. Of the non-trivial sets, one set showed considerably more consistency than the others, and this was used in SAP4B for the determination of signs of most of the remainder of the 328 reflections having $|E| \geqslant 1{\cdot}40$. An E-map of 316 of these reflections showed clearly the whole of the sodium complex, thirty-nine non-hydrogen atoms.

The structure was refined by block-diagonal least-squares methods, with the scattering factors of ref. 4 and with minimisation of $\Sigma w(F_o - F_c)^2$. Initially, w was calculated from the counting data: $w_c = 1/\sigma_c^2$ where $\sigma_c^2 = \sigma_I^2/(4 . I . Lp)$ and Lp is the Lorentz-polarisation factor. The temperature factors of the sodium ion and the four atoms of the substituent groups of the *o*-nitrophenolate ion were refined anisotropically; the other atoms were treated isotropically. All the hydrogen atoms were located in a Fourier-difference map and, with scattering factors of ref. 5, their parameters were included in later cycles of refinement. The weighting of reflections was adjusted so that mean values of $w(F_o - F_c)^2$ approached unity over several ranges of F_o; in the final cycles of refinement, by full-matrix least-squares methods, $w = w_c/(0{\cdot}335 + 0{\cdot}0416|F_o| + 0{\cdot}00890|F_o|^2)$. Refinement was concluded with R 0·124 for all data, 0·074 for observed data only.

Final atomic parameters are in Table 2. Measured and calculated structure factors for both complexes are listed in Supplementary Publication No. SUP 20758 (27 pp. 1 microfiche).*

o-Nitrophenolatobis-(1,10-*phenanthroline*)*rubidium*

The rubidium complex was found to decompose on exposure to air for long periods. A single crystal, of poorly defined shape, *ca.* 0·35 × 0·20 × 0·17 mm³ was mounted in a sealed glass capillary tube.

The procedures for collection of the intensity data and for their reduction to structure amplitudes were as for the sodium complex.

Crystal Data.—$C_{30}H_{20}N_5O_3Rb$, $M = 584{\cdot}00$, Triclinic, $a = 11{\cdot}413(6)$, $b = 13{\cdot}214(6)$, $c = 10{\cdot}068(15)$ Å, $\alpha = 99{\cdot}06(5)$, $\beta = 114{\cdot}80(5)$, $\gamma = 101{\cdot}78(3)^\circ$, $U = 1297{\cdot}6$ Å³, $D_m = 1{\cdot}48$ (flotation in CCl_4–light petroleum, b.p. 60—80 °C), $Z = 2$, $D_c = 1{\cdot}494$, $F(000) = 592$. $\mu(\text{Mo-}K_{\bar{\alpha}}) = 20{\cdot}7$ cm⁻¹. Space group $P\bar{1}$.

TABLE 2

Final atomic co-ordinates (fractional ×10⁴) and thermal parameters (B Å², U Å² × 10⁴) of *o*-nitrophenolatobis-1,10-phenanthroline)sodium; standard deviations are in parentheses

	x	*y*	*z*	*B*
Na	4411(3)	2645(3)	2519(2)	*
N(1)	5135(6)	2679(6)	1040(4)	3·75(12)
C(2)	4436(9)	1418(9)	282(6)	4·93(19)
C(3)	4574(9)	1485(9)	−628(5)	5·26(19)
C(4)	5476(9)	2924(9)	−750(5)	4·82(18)
C(5)	7198(9)	5864(9)	−70(5)	5·11(18)
C(6)	7919(8)	7124(8)	663(5)	4·49(17)
C(7)	8517(9)	8331(9)	2403(6)	5·72(20)
C(8)	8300(10)	8152(10)	3238(6)	6·37(22)
C(9)	7302(9)	6596(10)	3306(6)	5·60(20)
N(10)	6571(6)	5311(6)	2564(4)	4·12(12)
C(11)	6826(7)	5505(7)	1722(5)	3·77(15)
C(12)	6075(7)	4141(7)	914(4)	3·31(14)
C(13)	6256(8)	4295(8)	5(5)	3·93(15)
C(14)	7801(8)	7032(8)	1601(5)	4·85(17)
H(2)	3748(69)	498(65)	410(40)	6·2(18)
H(3)	3810(71)	416(69)	−1063(42)	7·2(21)
H(4)	5648(87)	3013(83)	−1405(51)	11·3(24)
H(5)	7234(63)	5693(60)	−725(37)	5·2(21)
H(6)	8702(95)	8407(92)	569(54)	13·3(26)
H(7)	9349(94)	9378(89)	2274(54)	12·5(26)
H(8)	8693(88)	8849(81)	3793(48)	9·6(22)
H(9)	6889(78)	6452(74)	3811(45)	8·5(22)
N(21)	3446(7)	−144(6)	2407(4)	4·45(13)
C(22)	2087(9)	−1285(9)	1745(5)	5·43(19)
C(23)	1421(10)	−2933(10)	1701(6)	6·06(21)
C(24)	2209(9)	−3316(9)	2367(6)	5·52(20)
C(25)	4563(9)	−2479(9)	3799(5)	5·02(18)
C(26)	5878(9)	−1331(9)	4475(5)	5·20(19)
C(27)	7908(10)	1556(10)	5234(5)	5·58(20)
C(28)	8388(9)	3064(9)	5236(6)	5·72(20)
C(29)	7511(9)	3379(9)	4518(5)	4·95(18)
N(30)	6197(6)	2231(6)	3808(4)	4·39(13)
C(31)	5669(7)	691(7)	3796(4)	3·79(15)
C(32)	4236(8)	−535(7)	3067(4)	3·78(15)
C(33)	3645(8)	−2158(8)	3054(5)	4·41(16)
C(34)	6512(8)	316(8)	4515(5)	4·49(16)
H(22)	1605(94)	−758(89)	1380(54)	12·6(26)
H(23)	416(115)	−3563(116)	1148(66)	17·5(29)
H(24)	1808(90)	−4503(85)	2227(53)	11·5(25)
H(25)	3819(74)	−3700(73)	3606(42)	7·8(25)
H(26)	6515(85)	−1426(81)	5050(50)	10·5(24)
H(27)	8323(89)	1131(84)	5631(50)	10·8(23)
H(28)	9350(84)	4055(79)	5654(48)	9·7(22)
H(29)	7760(69)	4531(69)	4494(40)	6·8(17)
C(41)	1001(7)	2373(7)	1904(4)	3·10(14)
C(42)	845(7)	2632(6)	2836(4)	3·13(14)
C(43)	−362(9)	2749(8)	2974(5)	4·79(18)
C(44)	−1436(9)	2760(8)	2252(6)	5·21(19)
C(45)	−1329(8)	2565(8)	1325(5)	4·37(17)
C(46)	−195(8)	2361(8)	1158(5)	4·13(16)
N(47)	1932(7)	2687(6)	3658(4)	*
O(48)	1522(6)	2436(7)	4376(4)	*
O(49)	3211(6)	2933(6)	3671(3)	*
O(50)	2015(5)	2197(5)	1718(3)	*
H(43)	−359(58)	2940(55)	3586(34)	3·9(14)
H(44)	−2106(86)	3073(81)	2389(51)	10·1(23)
H(45)	−2041(80)	2560(74)	784(47)	9·1(20)
H(46)	−46(72)	2134(68)	526(44)	7·7(19)

* Anisotropic thermal parameters, in the form: $\exp[-2\pi^2 \cdot 10^{-4} (U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Na	519(18)	610(18)	615(18)	327(15)	272(15)	339(15)
N(47)	847(57)	821(48)	443(45)	572(47)	278(46)	274(36)
O(48)	1236(53)	1909(65)	690(40)	1068(50)	501(40)	652(42)
O(49)	924(47)	1565(58)	712(40)	884(47)	266(38)	453(36)
O(50)	781(36)	1105(41)	566(31)	697(34)	345(28)	366(28)

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

[4] 'International Tables for X-Ray Crystallography,' vol. III, p. 202, Kynoch Press, Birmingham, 1962.

[5] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

Twenty reflections were used in the determination of the cell parameters. The intensities of 2616 reflections were measured, and, by the same criteria as for the sodium complex, 2107 (80·5%) were considered observed.

Structure Analysis.—The co-ordinates of the rubidium ion were determined from the Patterson map, and those of the other non-hydrogen atoms from an electron-density map.

The course of refinement and location of the hydrogen atoms followed closely that of the sodium complex. The scattering factors, including corrections for anomalous dispersion, for the rubidium ion were from ref. 4; the cation and the same nitrogen and oxygen atoms were refined anisotropically. The final weighting scheme was $w = w_c/(1{\cdot}73 - 0{\cdot}181|F_o| + 0{\cdot}0158|F_o|^2)$. At the conclusion, R was 0·067 for all data, 0·051 for observed data only. In a final Fourier-difference synthesis, the five strongest peaks, 0·4—0·5 eÅ^{-3} were found midway between bonded atoms.

Final atomic parameters are in Table 3.

Computing.—The full-matrix least-squares refinement by the programme NUCLS, and the succeeding determination of statistical errors from the full correlation matrix by ORFFE, were computed on the IBM 360/65I system of University College, London.[6] The remainder of the computing in these structure analyses was done on the IBM 1130 of this laboratory, with the *X*-RAY ARC series of programmes; in addition to the programmes listed in ref. 7, this library includes ECALC (normalisation of the structure amplitudes) by P. R. Mallinson, and the series SAP3, SAP4A, and SAP4B (phase determination in the centrosymmetric case, by the symbolic-addition method) by S. R. Hall and F. R. Ahmed, adapted for the 1130 system by B. L. Vickery; a multisolution option was added to SAP4A for convenience in use with crystals of space group $P\bar{1}$).

DISCUSSION

The atomic numbering schemes and the molecular dimensions of the complexes are shown in Figures 1 and 2. Details of the mean planes through portions of the complexes are in Table 4.

The crystal structures of the sodium and rubidium complexes are similar in many aspects. The principal difference between the structures arises from the sizes of the cations and from their co-ordination capacities. In the sodium complex, the cation is six-co-ordinate, surrounded by the three chelating ligands in pseudo 32 symmetry (Figure 3), and this unit exists as an entity in the crystal. The rubidium ion, in its complex, has a similar pseudo-three-fold symmetry of ligands, but, having a larger co-ordination sphere, it can accept co-ordination from the outer oxygen atom, O(48), of the nitro-group of a neighbouring *o*-nitrophenolate ion (Figure 4).

Thus the rubidium ion (and presumably the potassium and caesium ions in their isostructural complexes) is seven-co-ordinate, and this complex exists, in crystal form, as dimer entities, the two cations bridged by *o*-nitrophenolate groups about a centre of symmetry, (diagrammatically shown in Figure 5).

TABLE 3

Final atomic co-ordinates (fractional ×10^4) and thermal parameters (B Å^2, U Å^2 × 10^4) of *o*-nitrophenolatobis-(1,10-phenanthroline)rubidium; standard deviations are in parentheses

	x	*y*	*z*	*B*
Rb	2014(1)	1813(1)	626(1)	*
N(1)	4418(5)	3863(4)	2066(6)	4·25(12)
C(2)	4336(8)	4629(7)	1305(9)	5·21(17)
C(3)	5187(9)	5661(7)	1923(10)	5·57(18)
C(4)	6162(9)	5963(7)	3361(10)	5·41(19)
C(5)	7310(7)	5494(6)	5820(8)	4·61(16)
C(6)	7385(8)	4779(6)	6628(9)	4·57(16)
C(7)	6538(8)	2930(6)	6750(9)	4·76(16)
C(8)	5654(8)	1914(6)	6072(9)	5·04(17)
C(9)	4707(7)	1688(6)	4534(8)	4·73(16)
N(10)	4599(5)	2386(4)	3686(6)	4·22(12)
C(11)	5483(6)	3381(5)	4392(7)	3·32(13)
C(12)	5406(6)	4166(5)	3544(7)	3·44(13)
C(13)	6315(7)	5206(5)	4251(8)	4·02(14)
C(14)	6488(6)	3696(5)	5933(7)	3·62(14)
H(2)	3553(64)	4224(48)	333(73)	5·8(16)
H(3)	5124(110)	6131(84)	1491(119)	15·4(38)
H(4)	6741(48)	6584(39)	3954(54)	2·3(12)
H(5)	7867(65)	6304(53)	6349(71)	6·3(17)
H(6)	7965(86)	4810(66)	7636(96)	10·3(26)
H(7)	7132(85)	3165(66)	7812(93)	10·4(25)
H(8)	5606(61)	1249(49)	6565(69)	5·7(16)
H(9)	3988(57)	851(47)	3900(64)	4·8(14)
N(21)	1043(6)	2349(4)	−2418(6)	4·52(12)
C(22)	321(8)	3039(6)	−2609(9)	5·51(18)
C(23)	−348(8)	3264(6)	−4011(9)	5·60(18)
C(24)	−279(8)	2732(6)	−5245(10)	5·09(17)
C(25)	493(8)	1356(6)	−6376(9)	4·81(16)
C(26)	1180(7)	644(6)	−6191(8)	4·85(16)
C(27)	2602(8)	−298(7)	−4508(10)	5·36(19)
C(28)	3270(8)	−412(6)	−3087(9)	5·53(18)
C(29)	3192(8)	206(6)	−1909(10)	5·33(18)
N(30)	2527(5)	944(4)	−2023(6)	4·07(12)
C(31)	1859(6)	1057(5)	−3449(7)	3·76(14)
C(32)	1100(6)	1817(5)	−3640(7)	3·64(14)
C(33)	438(7)	1979(5)	−5109(7)	4·10(14)
C(34)	1878(7)	457(5)	−4734(8)	4·19(15)
H(22)	284(78)	3385(60)	−1522(89)	9·8(23)
H(23)	−835(76)	3861(61)	−4062(87)	9·6(22)
H(24)	−679(69)	2768(53)	−6242(80)	7·2(19)
H(25)	131(78)	1572(60)	−7335(89)	9·1(22)
H(26)	1227(64)	105(50)	−7179(73)	6·5(17)
H(27)	2457(63)	−663(49)	−5368(72)	5·7(17)
H(28)	3715(92)	−1123(73)	−2915(102)	13·8(30)
H(29)	3533(69)	301(54)	−740(84)	7·6(19)
C(41)	−924(7)	2921(5)	710(7)	3·78(14)
C(42)	−2031(6)	1979(5)	116(7)	3·37(13)
C(43)	−3253(8)	1975(6)	157(9)	4·56(16)
C(44)	−3375(9)	2914(7)	822(10)	5·65(19)
C(45)	−2334(8)	3840(7)	1398(9)	5·24(17)
C(46)	−1162(8)	3863(6)	1341(8)	4·92(17)
N(47)	−1982(6)	970(4)	−558(6)	*
O(48)	−3042(5)	206(4)	−1328(6)	*
O(49)	−888(5)	828(4)	−381(6)	*
O(50)	208(5)	2982(4)	716(5)	*
H(43)	−3922(65)	1333(50)	−404(72)	5·7(17)
H(44)	−4060(87)	2837(68)	960(99)	9·6(27)
H(45)	−2385(62)	4570(50)	1922(69)	6·2(16)
H(46)	−399(56)	4552(45)	1609(59)	4·4(13)

* Anisotropic parameters: as defined in Table 2.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rb	464(5)	665(5)	467(5)	181(4)	174(4)	152(4)
N(47)	553(43)	554(43)	420(37)	154(38)	149(34)	127(32)
O(48)	661(37)	544(33)	862(40)	71(30)	152(32)	30(30)
O(49)	677(38)	680(36)	834(39)	265(30)	315(31)	−20(28)
O(50)	645(34)	604(32)	783(36)	137(26)	327(29)	65(27)

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[6] IBM 360 programs: NUCLS by R. J. Doedens and J. A. Ibers; ORFFE by W. R. Busing, K. O. Martin, and H. A. Levy.

[7] D. L. Hughes and M. R. Truter, *J.C.S. Dalton*, 1972, 2214.

TABLE 4

Mean planes

(*a*) Equations of mean planes in the form $lX' + mY' + nP' = p$, where X', Y', Z' are co-ordinates (Å) referred to orthogonal axes parallel to the *a* axis, in the (*a*, *b*) plane and parallel to the *c** axis

Plane No.	Atoms of the plane	*l*	*m*	*n*	*p*
(i) Phenanthroline ligands					
(1)	Na complex, molecule (A)	−0·9461	0·1710	−0·2749	−3·5362
(2)	Na complex, molecule (B)	0·7978	0·1179	−0·5912	0·1131
(3)	Rb complex, molecule (A)	0·9347	−0·2114	−0·2853	1·4549
(4)	Rb complex, molecule (B)	−0·6943	−0·6928	−0·1944	−3·2310
(5)	Outer ring (I),* molecule (A), Na complex	−0·9469	0·1748	−0·2697	−3·5333
(6)	Outer ring (I),* molecule (B), Na complex	0·7850	0·0956	−0·6120	0·0533
(7)	Outer ring (I),* molecule (A), Rb complex	0·9315	−0·1969	−0·3056	1·4723
(8)	Outer ring (I),* molecule (B), Rb complex	−0·6841	−0·6952	−0·2202	−3·1385
(9)	Centre ring (II),* molecule (A), Na complex	−0·9515	0·1615	−0·2617	−3·5906
(10)	Centre ring (II),* molecule (B), Na complex	0·8028	0·1120	−0·5856	0·1954
(11)	Centre ring (II),* molecule (A), Rb complex	0·9376	−0·2134	−0·2742	1·5171
(12)	Centre ring (II),* molecule (B), Rb complex	−0·7037	−0·6839	−0·1922	−3·2481
(13)	Outer ring (III),* molecule (A), Na complex	−0·9398	0·1866	−0·2861	−3·4780
(14)	Outer ring (III),* molecule (B), Na complex	0·8085	0·1375	−0·5721	0·2725
(15)	Outer ring (III),* molecule (A), Rb complex	0·9352	−0·2233	−0·2745	1·4773
(16)	Outer ring (III),* molecule (B), Rb complex	−0·7090	−0·6836	−0·1729	−3·3396
(ii) *o*-Nitrophenolate ions					
(17)	Benzene ring, C(41)—(46); Na complex	−0·0953	−0·9778	−0·1862	−1·7052
(18)	Benzene ring, C(41)—(46); Rb complex	−0·0356	0·4551	−0·8896	1·1659
(19)	C(41)—(43), N(47); Na complex	−0·0773	−0·9820	−0·1719	−1·6838
(20)	C(41)—(43), N(47); Rb complex	−0·0264	0·4517	−0·8917	1·1278
(21)	C(42), N(47), O(48), O(49); Na complex	0·1738	−0·9152	−0·3633	−2·7363
(22)	C(42), N(47), O(48), O(49); Rb complex	0·2020	0·5328	−0·8217	0·6797

(*b*) Deviations (Å) from the mean planes

Plane No.	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
N(**1**) *	−0·004	0·021	0·003	0·025	0·005	0·000	0·004	−0·006
C(**2**)	−0·004	−0·020	−0·037	0·052	−0·004	0·003	−0·005	0·014
C(**3**)	0·000	−0·051	−0·037	0·007	−0·005	0·003	−0·000	−0·003
C(**4**)	0·005	−0·051	−0·009	−0·034	0·004	−0·013	0·001	−0·008
C(**5**)	0·035	0·015	0·005	−0·005				
C(**6**)	0·017	0·001	−0·017	0·009				
C(**7**)	−0·023	−0·012	−0·021	0·047				
C(**8**)	−0·010	−0·049	−0·028	0·019				
C(**9**)	0·013	−0·041	−0·008	−0·009				
N(**10**)	0·027	0·014	0·013	−0·038				
C(**11**)	−0·013	0·031	0·014	−0·011				
C(**12**)	−0·020	0·029	0·022	−0·005	−0·007	−0·007	−0·005	0·001
C(**13**)	−0·006	0·018	0·026	−0·030	0·003	0·012	0·002	0·006
C(**14**)	−0·026	0·011	0·007	0·019				
Na	0·529 †	−0·106 †						
Rb			−0·631 †	0·535 †				

Plane No.	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)
C(**5**)	0·014	0·007	0·002	0·002				
C(**6**)	0·003	−0·003	−0·011	0·000				
C(**7**)					0·006	0·012	−0·002	0·005
C(**8**)					−0·005	−0·001	−0·002	−0·004
C(**9**)					−0·007	−0·010	0·002	0·006
N(**10**)					0·007	0·006	0·001	−0·003
C(**11**)	0·013	0·004	−0·002	−0·011	−0·009	−0·002	−0·004	0·005
C(**12**)	−0·001	−0·001	−0·004	0·012				
C(**13**)	−0·010	−0·003	0·005	−0·008				
C(**14**)	−0·017	−0·003	0·008	0·006	0·003	−0·007	0·004	−0·004

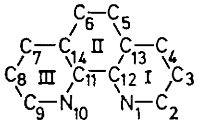
Plane No.	(17)	(18)	(19)	(20)	(21)	(22)
C(41)	0·010	−0·005	0·006	−0·000	0·440 †	0·294 †
C(42)	−0·022	−0·001	−0·018	0·001	0·002	−0·001
C(43)	0·027	0·010	0·009	−0·001	−0·348 †	−0·324 †
C(44)	−0·001	−0·008				
C(45)	−0·016	−0·004				
C(46)	0·008	0·011				
N(47)	−0·031 †	−0·014 †	0·005	−0·000	−0·008	0·004
O(48)	0·339 †	0·251 †	0·382 †	0·262 †	0·002	−0·001
O(49)	−0·356 †	−0·299 †	−0·299 †	−0·274 †	0·002	−0·001
O(50)	0·020 †	−0·020 †				
Na	−0·443 †					
Rb		−0·714†				

TABLE 4 (*Continued*)

(*c*) Angles (°) between planes:

	Na Complex				Rb Complex			
	(i) Phenantholine ligands							
	Molecule (A)		Molecule (B)		Molecule (A)		Molecule (B)	
Planes	(1)–(5)	0·4	(2)–(6)	1·9	(3)–(7)	1·4	(4)–(8)	1·6
	(1)–(9)	1·0	(2)–(10)	0·5	(3)–(11)	0·7	(4)–(12)	0·7
	(1)–(13)	1·2	(2)–(14)	1·7	(3)–(15)	0·9	(4)–(16)	1·6
	(5)–(9)	0·9	(6)–(10)	2·0	(7)–(11)	2·1	(8)–(12)	2·1
	(5)–(13)	1·2	(6)–(14)	3·6	(7)–(15)	2·3	(8)–(16)	3·1
	(9)–(13)	2·1	(10)–(14)	1·7	(11)–(15)	0·6	(12)–(16)	1·1
	(ii) *o*-Nitrophenolate ions							
	(19)–(21)	18·6			(20)–(22)	14·5		

* The atoms and rings of the phenanthroline molecules are numbered:



Bold arabic atom numbers in parentheses refer to this general formula; ordinary arabic numbers refer to the atoms of Figures 1 and 2.

† Atoms not used in calculation of planes.

Environment of the Alkali-metal Cations.—The co-ordination pattern of the three ligands, arranged as propellor blades in pseudo 32 symmetry about the sodium ion, is similar to that in another trichelate sodium complex $NaClO_4[(salen)Cu]_2,0·5xylene$.[8] In the majority of its complexes,[9] sodium is surrounded by an octahedral arrangement of ligating atoms, but with large chelating ligands, such an arrangement may not be sterically feasible. Each phenanthroline molecule is chelated through the two nitrogen atoms to the sodium ion; the nitrogen atoms of molecule (A) [atoms numbered (1)—(14)], are almost equidistant from the cation (2·491 and 2·506 Å), but in molecule (B) [atoms (21)—(34)] the Na · · · N distances differ (2·444 and 2·557 Å), probably a result of steric effects. The *o*-nitrophenolate ion is co-ordinated through the phenolic oxygen O(50) and one of the nitro-group oxygen atoms, O(49) with Na · · · O 2·281 and 2·421 Å.

Figure 3 is a projection of the monomeric unit on the plane of N(1), N(21), and O(50); the projection on the plane through the lower three co-ordinating atoms, N(10), N(30), and O(49) is very similar, and the sodium ion lies approximately equidistant from these planes.

In the rubidium complex, the corresponding dimensions about the cation are: Rb · · · N 3·059 and 3·082 Å in phenanthroline molecule (A), and 3·046 and 3·065 Å in molecule (B); Rb · · · O(50) is 2·838 and Rb · · · O(49) 2·949 Å. The extra interaction of the rubidium ion, with O(48) of the centrosymmetrically related unit of the dimer, has Rb · · · O 3·190 Å, a rather weaker interaction than the others.

Figure 4 is the corresponding projection for the rubidium complex; O(48*) is shown close to the pseudo-triad axis. The rubidium ion is 1·81 Å from the plane of the projection, but only 0·52 Å from the plane of N(10), N(30), and O(49), showing the considerable distortion (from the sodium complex arrangement) which allows the inclusion of O(48*) in the co-ordination sphere.

The cations in both complexes are displaced by varying amounts from the mean planes of the ligands. In the sodium complex, the cation is 0·53 Å from the mean plane through phenanthroline molecule (A) [Table 4, plane (1)], and 0·11 Å from the plane through molecule (B), [plane (2)]. In the rubidium complex, the corresponding values are 0·63 and 0·53 Å [planes (3) and (4)], in the same directions as in the sodium complex (Figures 3 and 4).

The Phenanthroline Ligands.—The dimensions of the phenanthroline molecules in both complexes are very similar. The variation in bond lengths in each molecule agrees with that predicted by Pauling for the related phenanthrene molecule on the basis of resonance-structure contributions;[10] agreement is good, too, in general, with the dimensions of phenanthroline ligands of transition-metal complexes, tabulated in ref. 11. In particular, the C(**5**)–C(**6**) bonds (for the numbering system used for phenanthroline molecules generally, see footnote to Table 4) are shortest (1·304—1·334 Å), and the C(**5**)–C(**13**) type and C(**11**)–C(**12**) are longest (1·434—1·457 and 1·424—1·439 Å); the bonds involving nitrogen atoms are generally shorter than C–C bonds, with the N(**1**)–C(**2**) slightly shorter than the N(**1**)–C(**12**) type bonds. Bond angles vary significantly around the phenanthroline molecules; notably, the angles at the nitrogen atoms are somewhat less than 120° (115·7—119·1°) and at the neighbouring C(**2**) atoms somewhat more than 120° (122·5—125·6°).

All the phenanthroline molecules show considerable deviation from planarity, but there seems to be no characteristic pattern in the degree or direction of the

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[8] G. H. W. Milburn, M. R. Truter, and B. L. Vickery, *Chem. Comm.*, 1968, 1188, and Figure 4 of ref. 9.

[9] M. R. Truter, *Structure and Bonding*, 1973, **15** (in press).

[10] L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1967.

[11] B. A. Frenz and J. A. Ibers, *Inorg. Chem.*, 1972, **11**, 1109.

distortions. In general, the six-membered rings within the molecules are planar; the centre ring of molecule A of the sodium complex [Table 4, plane (9)] shows the most marked distortions with atomic displacements of up to 0·017 Å (*i.e.* 2σ) from the mean plane. The cations are displaced by varying amounts from the phenanthroline molecule planes, as described above.

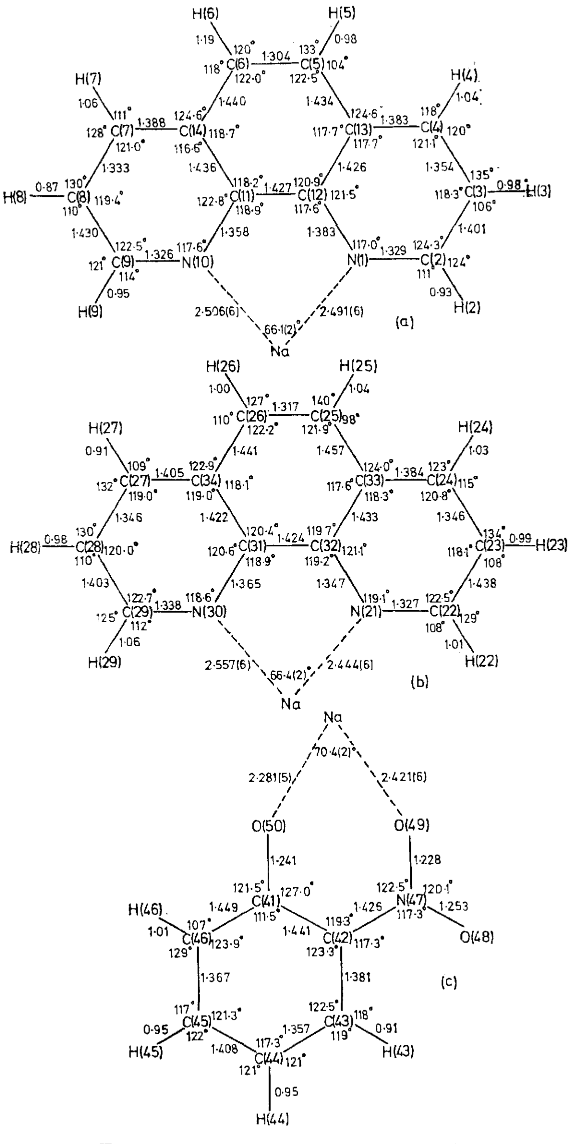


FIGURE 1 The atom numbering scheme and the molecular dimensions of the sodium complex: (a) phenanthroline molecule (A), (b) phenanthroline molecule (B), and (c) *o*-nitrophenolate ion. Mean σ, (i) ligand distances: C–C 0·008, C–N 0·007, C–O and N–O 0·006, C–H 0·06 Å; (ii) ligand angles: C–C–C 0·7°, angles involving C, N, and O atoms 0·6 °, angles involving H 4°

The o-*Nitrophenolate Ions*.—The dimensions of the *o*-nitrophenolate ions (Figures 1 and 2) are compared with those of related ions in Table 5.[12-14]

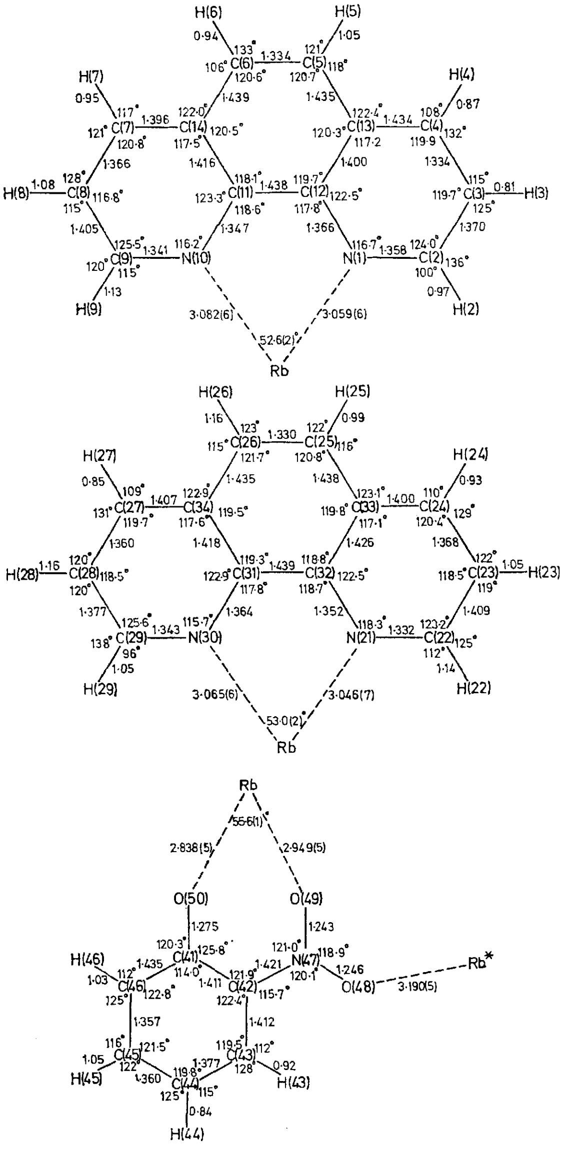
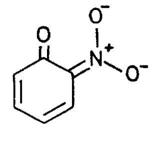


FIGURE 2 The atom numbering scheme and the molecular dimensions of the rubidium complex: (a) phenanthroline molecule (A), (b) phenanthroline molecule (B), (c) *o*-nitrophenolate ion. Mean σ (i) ligand distances: C–C 0·009, C–N 0·008, C–O 0·007, N–O 0·006, C–H 0·07 Å; (ii) the ligand angles: C–C–C 0·7°, angles involving C, N, and O atoms 0·6°, angles involving H 4°

The systematic variations in bond lengths and angles in these compounds may be explained in terms of (*a*) contributions of resonance forms to the molecular structure, and (*b*) the second-order hybridisation at the ring carbon atoms having substituent groups. The first effect takes account of the quinonoid resonance structure:



and predicts that the C(**3**)–C(**4**) and C(**5**)–C(**6**) (the numbering scheme is in Table 5) should be shorter than

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[12] J. P. G. Richards, *Z. Krist.*, 1961, **116**, 468.
[13] K. Maartmann-Moe, *Acta Cryst.*, 1969, **B25**, 1452.
[14] M. A. Bush and M. R. Truter, *J. Chem. Soc.* (*A*), 1971, 745.

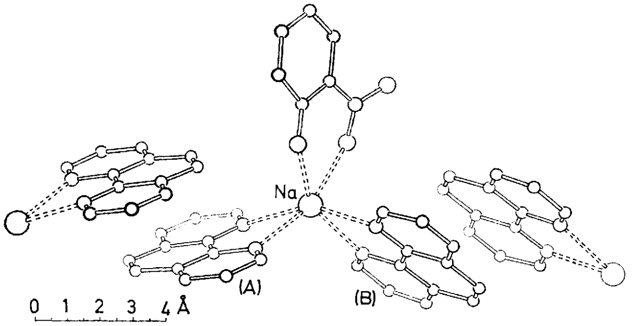


FIGURE 3 *o*-Nitrophenolatobis-(1,10-phenanthroline) sodium: one monomer unit, projected on the plane of N(1), N(21), and O(50) shown with two neighbouring phenanthroline ligands

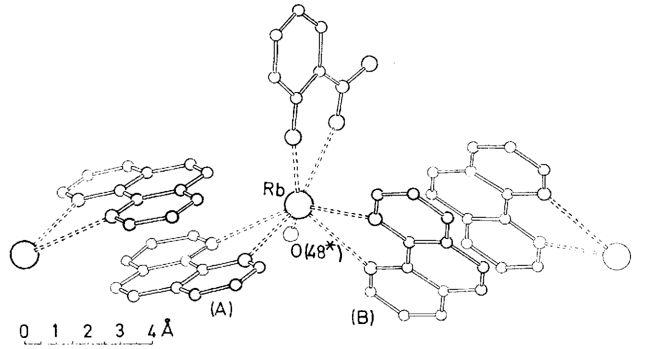
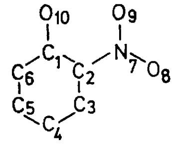


FIGURE 4 *o*-Nitrophenolatobis-(1,10-phenanthroline) rubidium: half the dimer unit and O(48*), projected on the plane of N(1), N(21), and O(50), shown with two neighbouring phenanthroline ligands

TABLE 5

Comparison of the dimensions (Å and deg.) of *o*-nitrophenolate and related ions. The atoms of the *o*-nitrophenolate ion are numbered:



Complex *	(1)	(2)	(3)	(4)	(5)	(6)
C(**1**)–C(**2**)	1·46	1·453	1·450	1·421	1·441	1·411
C(**2**)–C(**3**)	1·42	1·372	1·372	1·393	1·381	1·412
C(**3**)–C(**4**)	1·40			1·347	1·357	1·377
C(**4**)–C(**5**)	1·29			1·383	1·408	1·360
C(**5**)–C(**6**)	1·38			1·372	1·367	1·357
C(**6**)–C(**1**)	1·43			1·414	1·449	1·435
C(**1**)–C(**10**)	1·26	1·243	1·239	1·298	1·241	1·275
C(**2**)–N(**7**)	1·39	1·457	1·461	1·433	1·426	1·421
N(**7**)–O(**8**)	1·17	1·229	1·206	1·224	1·253	1·246
N(**7**)–O(**9**)	1·26	1·232	1·237	1·230	1·228	1·243
Av. σ(C–C)	0·04	0·006	0·005	0·006	0·008	0·009
Ring angle at C(**1**)	113	111·1	111·5	114·7	111·5	114·0
Ring angle at C(**2**)	122	124·9	124·2	121·7	123·3	122·4
Av. σ (angles)	2	0·5	0·4	0·4	0·6	0·6
NO_2 Rotation angle †	0	26·6	25·7	20·3	18·6	14·5
O(**9**) · · · O(**10**)	2·64	2·685	2·675	2·68	2·713	2·699

* Complexes: (1) Potassium *o*-nitrophenolate hemihydrate (ref. 12); (2) potassium picrate (ref. 13); (3) ammonium picrate (ref. 13); (4) isonitrosoacetophenone(*o*-nitrophenolato)-potassium (ref. 14); (5) and (6), present work Na and Rb complexes. † About C(**2**)–N(**7**) bond.

in benzene, and that the other ring bonds should be longer. Also the C(**1**)–O(**10**) and C(**2**)–N(**7**) bonds should be shorter than in phenol and nitrobenzene. These effects are apparent (Table 5) even though the nitro-groups are rotated about the C–C bond by at least 14°; in the picrates, where the angles of rotation are *ca.* 26° and where other resonance structures are possible, these effects are not so pronounced.

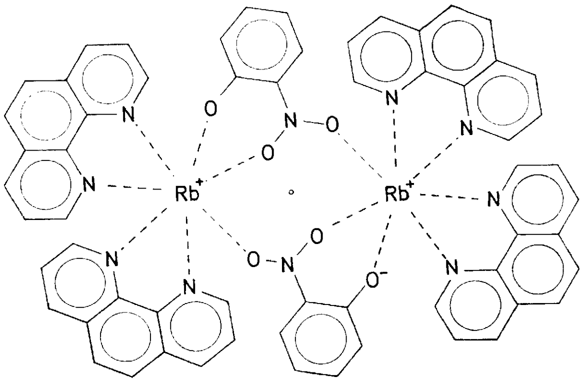


FIGURE 5 Diagrammatic representation of the co-ordination in a dimer unit of *o*-nitrophenolatobis-(1,10-phenanthroline) rubidium)

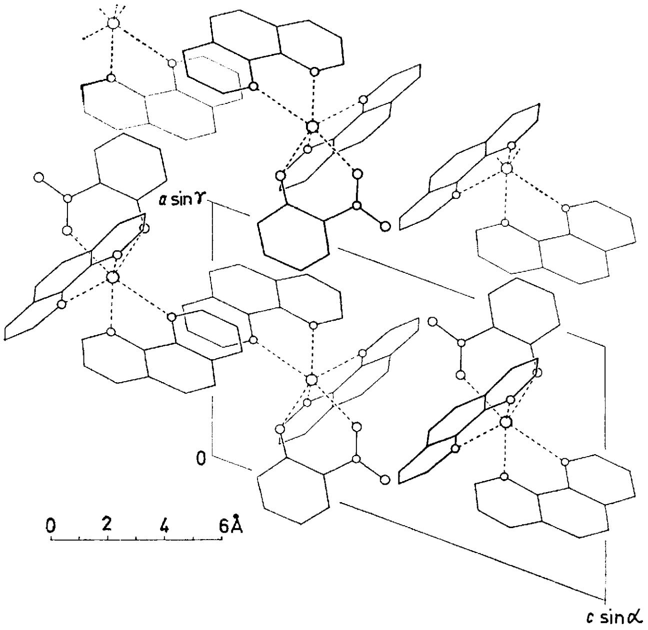


FIGURE 6 The packing arrangement of the sodium complex; a projection down the *b* axis

The electron-donating and -withdrawing properties of the phenolate oxygen atom and the nitro-group affect the hybridisation at the ring atoms C(**1**) and C(**2**),[15,16] and hence bond lengths and angles about these atoms. The shortening of the C(**1**)–O(**10**) bond enhances the

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[15] H. A. Bent, *J. Inorg. Nuclear Chem.*, 1961, **19**, 43.

[16] O. L. Carter, A. T. McPhail, and G. A. Sim., *J. Chem. Soc.* (*A*), 1966, 822.

resonance effect, but the lengthening of the C(**2**)–N(**7**) bond opposes it. In the ring, the effects of the two substituents are opposed in C(**1**)–C(**2**); C(**1**)–C(**6**) is lengthened (enhancing the resonance effect) and C(**2**)–C(**3**) is shortened (opposing the resonance effect). Also, the ring angles at C(**1**) and C(**2**) are notably decreased and increased from 120° by the hybridisation effects.

The benzene ring is not planar in the sodium complex; displacements from the mean plane are up to 0·027 Å, (*i.e.* 3·7σ) and the ring has a shallow, distorted boat conformation. The substituent atoms N(47) and O(50) are on opposite sides of the mean plane, the bond angles external to the ring at each of C(41) and C(42) differ considerably, and the nitro-group is rotated about the C–N bond by 18·6°; in this way the O(49) · · · O(50) distance is 2·713 Å, normal for non-interacting oxygen atoms.

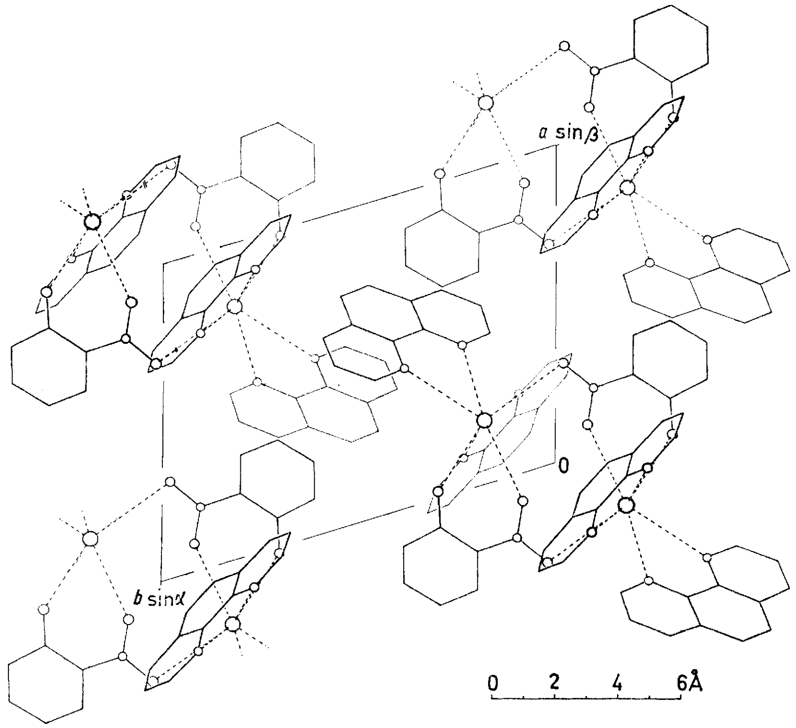

FIGURE 7 The packing arrangement of the rubidium complex; a projection down the *c* axis. The diagram has been orientated so that the arrangements, in projection, of this complex about the centres of symmetry may be compared with those of the sodium complex in Figure 6

Steric effects in the rubidium complex are less apparent. The oxygen atoms are still 2·699 Å apart, but the ring is less distorted from planarity (maximum displacement of the carbon atoms is 0·011 Å, 1·5σ) than in the sodium complex, the atoms N(47) and O(50) are on the same side of the ring mean plane, and the nitro-group is rotated 14·5° about C(42)–N(47). The co-ordination of O(48) to the second rubidium ion of the dimer presumably influences the delocalisation of electrons, and hence the dimensions, in the nitro group.

Packing Arrangements.—In both complexes, the packing of the phenanthroline molecules appears to determine the crystal structures. Figures **3** and **4** show pairs of phenanthroline molecules related by centres of symmetry. These pairs are each separated by normal van der Waals' distances for aromatic ring systems; the separations were determined from calculations of the distance of the centre of symmetry from the mean plane through the atoms involved in the overlap of the pairs of molecules. In the sodium complex, molecules (A) are separated by **3·33** Å, molecules (B) by **3·44** Å; in the rubidium complex the corresponding values are 3·42 and 3·50 Å.

The *o*-nitrophenolate ions do not have centrosymmetrically related neighbours in either complex. Their closest neighbours are atoms of phenanthroline molecules at van der Waals' distances.

The packing arrangements of the complexes are shown in Figures 6 and 7.

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[3/677 *Received, 2nd April,* 1973]