Quadridentate Schiff-base Metal Complexes as Chelating Ligands of Alkali Metals. Synthesis and Structure of Ammonium and Sodium Tetraphenylborate Addition Complexes with [*NN'*-Ethylenebis(salicylideneiminato)]nickel(II)

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Transition-metal complexes of the Schiff-base *NN'*-ethylenebis(salicylaldimine) (H_2salen) co-ordinate ammonium and alkali-metal cations to give addition complexes of different stoicheiometry. The complex [Ni(salen)] with ammonium or potassium tetraphenylborate, M'[BPh_4], gives addition compounds of formula [{Ni(salen}$_3$-M'(BPh_4)]·*n*L [L = solvent, *e.g.* tetrahydrofuran (thf), acetonitrile, or acetone]. For *n* = 2 and L = thf the complexes are isomorphous. Reaction with Na[BPh_4] in acetonitrile yields again a compound with Ni : Na 3 : 1, from which [{Ni(salen)}$_2$Na(NCMe)$_2$(BPh_4)]·2MeCN is obtained by very slow crystallization. The crystal structures of [{Ni(salen)}$_3$(NH_4)(BPh_4)]·2thf, (I), and [{Ni(salen)}$_2$Na(NCMe)$_2$]·2MeCN, (II), have been determined from three-dimensional *X*-ray data. Crystals of both compounds are triclinic, space group $P\bar{1}$, $Z = 2$, with cell parameters: (I), a = 18.93(1), b = 16.94(1), c = 14.84(1) Å, α = 91.6(2), β = 111.4(2), γ = 116.8(2)°; (II), a = 14.64(1), b = 15.56(1), c = 14.91 Å, α = 85.2(1), β = 114.2(1), γ = 98.7(1)°. The structures have been solved by Patterson and Fourier methods and refined by block-diagonal matrix least squares to *R* 0.11 for (I) and 0.080 for (II). The structure of (I) consists of discrete [BPh_4]$^-$ anions and [{Ni(salen)}$_3$(NH_4)]$^+$ macrocations in which the ammonium ion is surrounded by the six oxygen atoms (mean $NH_4^+ \cdots$ O 2.92 Å) of the three Ni(salen) moieties. The co-ordination polyhedron is intermediate between a trigonal prism and an octahedron, as determined by a balance of steric and electrostatic factors. Similarly the structure of (II) has discrete [BPh_4]$^-$ anions and [{Ni(salen)}$_2$Na(NCMe)$_2$]$^+$ macrocations with the sodium ion on an approximately two-fold axis, co-ordinated by the four oxygen atoms of the two Ni(salen) molecules and by the nitrogen atoms of the two acetonitrile molecules occupying *cis* positions. The co-ordination polyhedron approximates to an octahedron with mean $Na^+ \cdots$ O 2.41 and $Na^+ \cdots$ N 2.49 Å.

QUADRIDENTATE Schiff-base metal complexes can act as chelating agents of both transition- and non-transition-metal atoms,[1,2] including alkali and alkaline-earth metal ions.[3,4] Investigation of the complexes containing the last-named ions is of interest in connection with a more comprehensive view of the chemistry of d^0 cations [5] and with the influence of positive charges of the electronic properties of the transition-metal centre.[6]

Reaction of tetrahydrofuran (thf), acetone (L), and 1,2-dimethoxyethane (L_2) solutions of Na[BPh_4] with [*NN'*-ethylenebis(salicylideneiminato)]nickel(II), [Ni(salen)], gives complexes of formula [{Ni(salen)}$_2$NaL_2(BPh_4)]. Depending on the conditions of crystallization and drying, solids sometimes contain more solvent molecules.[4] For acetonitrile solutions a new complex was obtained of stoicheiometric formula [{Ni(salen)}$_3$Na(BPh_4)], which by very slow crystallization yielded [{Ni(salen)}$_2$Na(NCMe)$_2$(BPh_4)]·2MeCN, [ν(CN) at 2 260 cm^{-1}]. However, reaction between potassium or ammonium tetraphenylborate and [Ni(salen)] in acetone, thf, or MeCN gave solutions from which, when set aside, we always obtained crystals of [{Ni(salen)}$_3$M'(BPh_4)]·*n*L (M' = K or NH_4); *n* is a variable number of solvent molecules L, depending on drying conditions. The two complexes with L = thf and *n* = 2 are isomorphous.

Recently detailed structural information about the co-ordination of cations with many antibiotics and

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[1] E. Sinn and C. M. Harris, *Co-ordination Chem. Rev.*, 1969, **4**, 391; M. D. Hobday and T. D. Smith, *ibid.*, 1972, **9**, 311; C. A. Bear, J. M. Waters, and T. N. Waters, *J.C.S. Dalton*, 1974, 1059.

[2] M. Calligaris, L. Randaccio, R. Barbieri, and L. Pellerito, *J. Organometallic Chem.*, 1974, **76**, C56.

[3] S. J. Gruber, C. M. Harris, and E. Sinn, *J. Inorg. Nuclear Chem.*, 1968, **30**, 1805.

[4] C. Floriani, F. Calderazzo, and L. Randaccio, *J.C.S. Chem. Comm.*, 1973, 384.

[5] M. R. Truter, *Structure and Bonding*, 1973, **16**, 71.

[6] G. Costa, A. Puxeddu, and E. Reisenhofer, *Bioelectrochem. and Bioenergetics*, 1974, **1**, 29; C. Floriani and G. Fachinetti, *J.C.S. Chem. Comm.*, 1974, 615.

synthetic macrocyclic compounds has been obtained,[5,7] while there are very few structural data available for such Schiff-base–metal complexes.[8-10]

In order to clarify the crystal structure of this new series of compounds and to obtain information about factors affecting the co-ordination geometry of the cations in compounds of different stoicheiometry, we have carried out crystal-structure determinations of [{Ni(salen)}$_3$(NH$_4$)(BPh$_4$)]·2thf, (I), and [{Ni(salen)}$_2$-Na(NCMe)$_2$(BPh$_4$)]·2MeCN, (II).

EXPERIMENTAL

(*a*) *Reaction of* [Ni(salen)] *with Ammonium and Potassium Tetraphenylborate.*—Solid [Ni(salen)] (0.5 g, 1.54 mmol) was added to a well stirred solution of [NH$_4$][BPh$_4$] (0.5 g, 1.49 mmol) in thf (50 cm^3). Rapid dissolution of the solid took place, even if incomplete. A few minutes after the addition, the suspension was filtered, and the red-orange solution set aside to give a red-orange crystalline solid (*ca.* 50%), which was washed (thf) and dried *in vacuo* {Found: C, 66.3; H, 5.50; N, 7.20; Ni, 13.25. Calc. for [{Ni(salen)}$_3$-(NH$_4$)(BPh$_4$)]: C, 65.85; H, 5.05; N, 7.45; Ni, 13.5%}. The filtrate gave more solid which was dissolved by gentle heating and allowed to cool slowly giving red-orange crystals suitable for structure determinations. The solid (0.5 g) loses thf easily on drying (45 mg by g.l.c.). Analysis of the dried solid gave results similar to those already reported (Found: C, 66.3; H, 5.40; N, 7.15; Ni, 13.4%). Acetonitrile and acetone can be used as solvents with identical results. The preparation of the potassium complex was carried out very similarly {Found: C, 64.95; H, 4.85; K, 2.80; N, 6.30; Ni, 13.20. Calc. for [{Ni(salen}$_3$-K(BPh$_4$)]: C, 64.8; H, 4.65; K, 2.90; N, 6.30; Ni, 13.25%}. The solid (0.6 g) obtained by slow crystallization lost thf on drying (50 mg by g.l.c.).

(*b*) *Reaction of* [Ni(salen)] *with Sodium Tetraphenylborate.*—Solid [Ni(salen)] (0.5 g, 1.54 mmol) was added to an acetonitrile (25 cm^3) solution of Na[BPh$_4$] (0.5 g, 1.46 mmol), and the suspension was stirred for at least 24 h. The solid rapidly changed colour and crystalline form. It was filtered off, washed (MeCN), and dried *in vacuo* (*ca.* 80%) {Found: C, 65.4; H, 4.80; N, 6.30; Ni, 13.4. Calc. for [{Ni(salen)}$_3$Na(BPh$_4$)]: C, 65.6; H, 4.70; N, 6.40; Ni, 13.45%}. The i.r. spectrum and thermal decomposition showed the solid to be free from MeCN.

The complex [{Ni(salen)}$_3$Na(BPh$_4$)] was suspended in acetonitrile (50 cm^3) containing Na[BPh$_4$] (0.5 g). The suspension was heated until there was partial dissolution of the solid. The filtrate was allowed to cool slowly and gave red-orange crystals of [{Ni(salen)}$_2$Na(NCMe)$_2$(BPh$_4$)]·2MeCN, [ν(CN)(Nujol) at 2 260 cm^{-1}]. The solid (0.3 g) easily loses MeCN on drying (44 mg, by g.l.c.). Analysis of the residue gave: C, 67.4; H, 4.80; N, 5.55; Ni, 11.95. Calc. for [{Ni(salen)}$_2$Na(BPh$_4$)]: C, 67.75; H, 4.85; N, 5.65; Ni, 11.9%. All syntheses were carried out under anhydrous conditions.

Crystal Data.—(I). $C_{80}H_{82}BN_7Ni_3O_8$, $M = 1\,456.5$, Triclinic, $a = 18.93(1)$, $b = 16.94(1)$, $c = 14.84(1)$ Å, $\alpha = 91.6(2)$, $\beta = 111.4(2)$, $\gamma = 116.8(2)°$, $U = 3\,851$ Å^3, D_m (by flotation) $= 1.33$, $Z = 2$, $D_c = 1.26$. Space group $P\bar{1}$. Mo-K_α radiation, $\lambda = 0.710\,7$ Å; μ(Mo-K_α) 7.85 cm^{-1}.

(II). $C_{64}H_{60}BN_8NaNi_2O_4$, $M = 1\,156.5$, Triclinic, $a = 14.64(1)$, $b = 15.56(1)$, $c = 14.91(1)$ Å, $\alpha = 85.2(1)$, $\beta = 114.2(1)$, $\gamma = 98.7(1)°$, $U = 3\,061$ Å^3, D_m (by flotation) $= 1.33$, $Z = 2$, $D_c = 1.25$. Space group $P\bar{1}$. μ(Mo-K_α) $= 6.77$ cm^{-1}.

Crystals removed from their mother liquor very rapidly became opaque and lost crystallinity, probably because of loss of solvent. It was therefore necessary to mount the crystals in glass capillaries completely filled with the mother liquor. It was thus possible to prevent decomposition during the whole of the data collection.

Cell parameters were determined from Weissenberg and precession photographs taken with the Co-K_α radiation and refined with an on-line single-crystal Siemens diffractometer by use of Mo-K_α radiation. The ammonium complex (I) has been found, by comparison of the diffraction patterns, to be isostructural with a potassium derivative.

Intensity Measurements.—Three-dimensional intensity data were collected for both complexes on a Siemens diffractometer by the θ—2θ scan procedure by use of Mo-K_α radiation to $2\theta_{\text{max.}}$ 34° for (I) and 42° for (II). Reflections having $I_o \leqslant 3\sigma(I_o)$ were rejected, the remainder being corrected for the Lorentz-polarization factor. A total of 1 523 (I) and 3 352 (II) independent reflections was collected. No correction for absorption was applied in view of the very small dimensions of the crystals.

Structure Determination and Refinement.—Both structures were solved by Patterson and Fourier methods assuming the centrosymmetric space group $P\bar{1}$. Refinement in space group $P1$ led to higher values of R. After isotropic block-diagonal matrix least-squares refinement of all the non-hydrogen atoms of the crystallographically independent formula unit [{Ni(salen)}$_3$(NH$_4$)(BPh$_4$)], a Fourier synthesis was calculated to locate the molecules of solvent of crystallization. Four thf molecules were found per unit cell; however, the peaks were rather low and broadened and it was not possible to distinguish between the oxygen and carbon atom positions. All the thf atoms were therefore treated as carbon and their atomic parameters were held constant in the subsequent refinement. No attempt was made to locate hydrogen atoms. Assignment of anisotropic temperature factors to the nickel atoms reduced R to 0.11. This value seemed satisfactory in view of the poor quality of the crystals which did not allow a more complete collection of diffraction intensities.

The structure determination of the sodium derivative, (II), was more accurate because of the better quality of the available crystals. Anisotropic refinement of all the non-carbon atoms, apart from the nitrogen atoms of the acetonitrile molecules of crystallization, gave a final R value of 0.080. In the least-squares refinement the function minimized was $\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2$, where $w = 1/(A + B|F_o| + C|F_o|^2)$, with A 24.0, B 1.0, and C 0.024 for (I), and A 10.0, B 1.0, and C 0.004 0 for (II).

The crystallographically independent [Ni(salen)] portions of complex (I) are labelled (A)—(C), and of (II) (A) and (B). The numbering scheme for the atoms of each [Ni(salen)] portion and [BPh$_4$]$^-$ is shown in Figure 1. The atoms of the two thf molecules are labelled T(1)—(10), while the two acetonitrile molecules of crystallization in

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[7] J. D. Dunitz, M. Dobler, P. Seiler, and R. P. Phizackerley, *Acta Cryst.*, 1974, **B30**, 2733.

[8] G. H. W. Milburn, M. R. Truter, and B. L. Vickery, *Chem. Comm.*, 1968, 1188; *J.C.S. Dalton*, 1974, 841.

[9] L. Randaccio, *Gazzetta*, 1974, **104**, 991.

[10] S. R. Holbrook and D. van der Helm, *Acta Cryst.*, 1975, **B31**, 1653.

(II) are N(3),C(29),C(30) and N(4),C(31),C(32). Final atomic parameters are listed in Tables 1 and 2 for (I) and Tables 3 and 4 for (II). The estimated standard deviations, in parentheses, were calculated from the residuals and the diagonal elements of the inverse matrix of the final least-squares cycle. Observed and calculated structure factors of the two complexes are listed in Supplementary Publication No. SUP 21766 (17 pp., 1 microfiche).* Atomic scattering factors were calculated according to ref. 11. Bond lengths and angles, averaged over all the chemically equivalent parts of the crystallographically independent units, are reported in Table 5 for both complexes, together with the standard deviation of the weighted average.

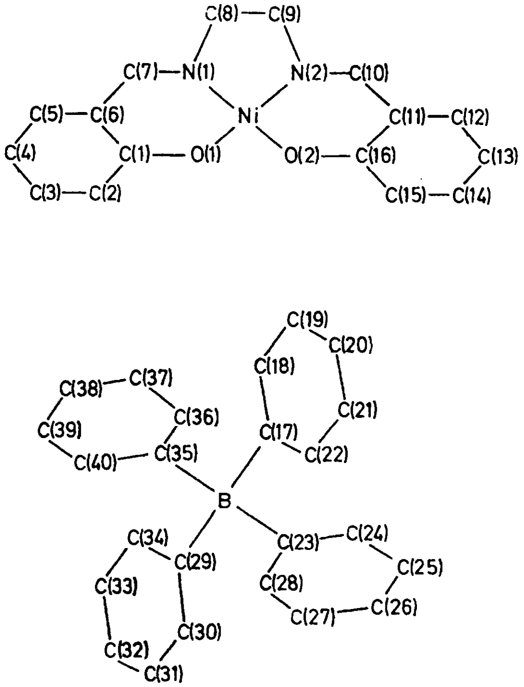

FIGURE 1 Numbering scheme for the [Ni(salen)(BPh$_4$)] unit

TABLE 1

Fractional co-ordinates ($\times 10^4$) and thermal factors (Å^2) for the three crystallographically independent [Ni(salen)] moieties of complex (I). Anisotropic temperature factors ($\times 10^4$) are in the form: $\exp -(B_{11}h^2 + B_{12}hk + B_{13}hl + B_{22}k^2 + B_{23}kl + B_{33}l^2)$. Estimated standard deviations are in parentheses

(*a*) Molecule (A)

	x	*y*	*z*	*B*
Ni	−3 388(4)	−3 904(4)	−373(4)	*
O(1)	−2 284(15)	−3 775(16)	317(19)	3.4(7)
O(2)	−3 270(17)	−3 527(18)	912(21)	4.7(8)
N(1)	−3 521(24)	−4 264(26)	−1 659(30)	6.7(12)
N(2)	−4 549(21)	−4 072(23)	−999(27)	5.6(11)
C(1)	−1 831(26)	−3 962(28)	23(32)	4.0(13)
C(2)	−1 019(28)	−3 870(31)	671(36)	5.8(14)
C(3)	−492(27)	−4 080(30)	362(34)	4.7(14)
C(4)	−716(31)	−4 331(34)	−660(39)	7.2(16)
C(5)	−1 550(30)	−4 484(33)	−1 408(38)	6.2(16)
C(6)	−2 088(26)	−4 278(29)	−1 106(34)	5.5(14)
C(7)	−2 945(23)	−4 328(25)	−1 827(29)	3.1(11)
C(8)	−4 240(33)	−4 175(36)	−2 438(42)	8.0(18)
C(9)	−4 950(37)	−4 432(41)	−2 227(47)	9.8(21)
C(10)	−5 002(29)	−3 966(32)	−747(38)	5.4(16)
C(11)	−4 759(29)	−3 662(32)	328(38)	7.3(16)
C(12)	−5 387(38)	−3 616(42)	706(50)	11.3(23)
C(13)	−5 117(40)	−3 266(45)	1 779(52)	11.5(24)
C(14)	−4 209(31)	−2 980(34)	2 418(40)	8.0(17)
C(15)	−3 581(28)	−3 046(30)	2 232(34)	5.2(14)
C(16)	−3 846(28)	−3 381(30)	1 129(35)	6.1(14)

* Anisotropic thermal parameters:

	B_{11}	B_{12}	B_{13}	B_{22}	B_{23}	B_{33}
Ni	39(3)	20(5)	20(5)	48(3)	−3(6)	28(4)

TABLE 1 (*Continued*)

(*b*) Molecule (B)

	x	*y*	*z*	*B*
Ni	−286(4)	167(5)	960(5)	†
O(1)	−1 451(18)	−762(19)	452(22)	5.3(9)
O(2)	28(15)	−694(17)	1 419(19)	4.4(7)
N(1)	−634(22)	1 062(24)	544(28)	6.0(11)
N(2)	911(22)	1 081(24)	1 404(27)	5.0(11)
C(1)	−2 238(28)	−783(31)	−132(36)	5.8(15)
C(2)	−3 065(32)	−1 560(35)	−491(41)	7.0(17)
C(3)	−3 839(31)	−1 527(34)	−1 051(39)	6.7(16)
C(4)	−3 672(31)	−720(34)	−1 187(39)	6.9(17)
C(5)	−2 974(28)	42(31)	−846(35)	6.1(15)
C(6)	−2 236(29)	113(33)	−325(37)	6.4(15)
C(7)	−1 473(31)	891(33)	11(38)	6.4(17)
C(8)	237(31)	1 942(33)	954(39)	6.0(17)
C(9)	971(30)	1 884(33)	959(38)	7.0(16)
C(10)	1 640(25)	1 024(28)	1 865(33)	4.5(13)
C(11)	1 618(26)	320(28)	2 208(33)	4.9(13)
C(12)	2 426(28)	318(30)	2 702(35)	5.6(14)
C(13)	2 418(29)	−444(31)	3 103(36)	7.0(15)
C(14)	1 675(32)	−1 298(35)	2 821(41)	6.7(17)
C(15)	873(26)	−1 323(29)	2 154(33)	5.3(11)
C(16)	791(25)	−613(28)	1 898(32)	4.3(13)

† Anisotropic thermal parameters:

	B_{11}	B_{12}	B_{13}	B_{22}	B_{23}	B_{33}
Ni	69(3)	26(5)	69(5)	46(3)	5(6)	50(4)

(*c*) Molecule (C)

	x	*y*	*z*	*B*
Ni	283(4)	−204(4)	4 059(5)	‡
O(1)	−846(15)	−379(17)	3 248(19)	4.4(7)
O(2)	−282(16)	−1 452(17)	3 732(19)	3.7(8)
N(1)	819(22)	1 085(24)	4 412(27)	5.4(11)
N(2)	1 410(23)	−132(25)	4 871(29)	5.7(12)
C(1)	−960(23)	277(25)	3 013(29)	2.6(12)
C(2)	−1 819(26)	37(29)	2 344(33)	5.0(14)
C(3)	−2 148(31)	607(33)	2 036(39)	6.6(17)
C(4)	−1 599(28)	1 509(32)	2 387(37)	6.6(15)
C(5)	−720(31)	1 858(34)	2 981(40)	7.5(17)
C(6)	−344(28)	1 267(30)	3 349(35)	6.5(15)
C(7)	458(28)	1 576(30)	4 086(35)	5.8(14)
C(8)	1 734(27)	1 499(30)	5 327(35)	5.5(14)
C(9)	2 096(31)	892(34)	5 209(39)	6.9(17)
C(10)	1 571(31)	−743(33)	5 117(39)	7.6(17)
C(11)	974(27)	−1 703(30)	4 799(34)	4.9(14)
C(12)	1 249(28)	−2 322(30)	5 175(35)	5.9(15)
C(13)	736(27)	−3 199(29)	4 864(34)	4.8(13)
C(14)	−133(28)	−3 478(30)	4 209(35)	5.2(14)
C(15)	−504(23)	−2 942(25)	3 831(30)	3.1(12)
C(16)	60(22)	−1 952(24)	4 099(27)	2.4(11)

‡ Anisotropic thermal parameters:

	B_{11}	B_{12}	B_{13}	B_{22}	B_{23}	B_{33}
Ni	54(3)	22(5)	32(5)	49(3)	2(6)	36(4)

Calculations.—All the calculations were made on a CDC 6200 computer, with programs described in ref. 12. A local program was used to obtain best molecular planes, whose equations were calculated according to ref. 13.

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* For details see Notices to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue.

[11] F. H. Moore, *Acta Cryst.*, 1963, **16**, 1169.

[12] V. Albano, A. Domenicano, and A. Vaciago, *Gazzetta*, 1966, **96**, 922.

[13] V. Schomaker, J. Waser, R. F. Marsh, and G. Bergman, *Acta Cryst.*, 1959, **12**, 600.

RESULTS AND DISCUSSION

Description of the Structures.—Structure of (I). The results show that the [Ni(salen)] molecules and the $[NH_4]^+$ ions are arranged in the crystal so that each ammonium ion is surrounded by three molecules of the metal complex with the six oxygen atoms nearly equidistant from the central nitrogen atom (Figure 2). The co-ordination polyhedron of the ammonium ion may be described as a trigonal prism distorted towards antiprismatic geometry by rotation of one triangular face through 26° with respect to the opposite one (Figure 3). The $NH_4^+ \cdots O$ distances range from 2.74 to 2.99(4) Å and may be indicative of weak hydrogen bonds. On the other hand the arrangement of the oxygen atoms around the ammonium ion is such that its four hydrogen atoms cannot all be involved at the same time in hydrogen bonds, suggesting the possibility of free rotation for the $[NH_4]^+$.

The mean values of the bond lengths and angles in the [Ni(salen)] moiety are in fairly good agreement with those found previously in similar complexes [2,14,15] and in (II). The differences should not be regarded as being chemically significant because of the low accuracy of the structure determination of (I). The co-ordination around the nickel atoms is nearly square planar, the four donor atoms being coplanar with the metal atom to

TABLE 2

Fractional co-ordinates ($\times 10^4$) and thermal factors ($Å^2$) of $(NH_4)(BPh_4)\cdot 2(thf)$ portion of complex (I). Estimated standard deviations are in parentheses

	x	*y*	*z*	*B*
N	−1 436(21)	−2 016(23)	1 768(26)	4.4(10)
B	−2 786(30)	4 537(33)	5 079(38)	3.8(15)
C(17)	−2 722(23)	4 568(25)	3 899(29)	3.6(12)
C(18)	−2 794(23)	5 189(25)	3 269(29)	3.0(12)
C(19)	−2 680(27)	5 157(29)	2 330(34)	4.9(14)
C(20)	−2 498(28)	4 536(31)	2 038(36)	5.9(15)
C(21)	−2 497(30)	3 863(33)	2 608(39)	6.4(17)
C(22)	−2 494(31)	3 894(34)	3 595(39)	7.0(17)
C(23)	−3 635(25)	3 660(27)	5 017(31)	3.8(12)
C(24)	−4 339(29)	2 961(31)	3 982(37)	6.3(15)
C(25)	−5 171(31)	2 159(34)	4 087(40)	7.8(17)
C(26)	−5 212(35)	2 139(38)	4 965(45)	9.0(20)
C(27)	−4 633(28)	2 748(31)	5 864(36)	5.4(15)
C(28)	−3 859(27)	3 480(29)	5 877(35)	5.5(14)
C(29)	−1 904(23)	4 597(25)	5 885(29)	3.1(11)
C(30)	−1 118(29)	5 288(32)	5 991(37)	6.4(15)
C(31)	−280(29)	5 446(32)	6 527(37)	6.4(16)
C(32)	−267(29)	4 822(31)	7 133(35)	6.1(15)
C(33)	−1 008(27)	4 086(29)	7 084(34)	4.7(14)
C(34)	−1 902(23)	3 932(26)	6 430(30)	3.6(12)
C(35)	−2 873(30)	5 409(32)	5 327(37)	7.3(16)
C(36)	−3 763(28)	5 354(31)	4 991(35)	5.4(14)
C(37)	−3 900(24)	6 104(25)	5 141(29)	2.9(11)
C(38)	−3 194(24)	6 928(26)	5 848(31)	3.6(12)
C(39)	−2 375(24)	6 996(26)	6 345(31)	3.7(12)
C(40)	−2 201(22)	6 260(24)	6 107(27)	2.0(11)
T(1)	−2 900	2 600	−100	
T(2)	−2 400	2 650	−1 400	
T(3)	−1 900	2 600	−900	
T(4)	−2 000	3 300	0	
T(5)	−2 800	3 250	−600	
T(6)	−4 400	400	3 200	
T(7)	−4 000	−200	3 700	
T(8)	−3 600	200	4 200	
T(9)	−3 600	1 000	4 500	
T(10)	−4 000	1 000	3 800	

TABLE 3

Fractional co-ordinates ($\times 10^4$) and thermal factors ($Å^2$) for the two crystallographically independent [Ni(salen)] moieties of complex (II). Anisotropic temperature factors ($\times 10^4$) are as in Table 1; estimated standard deviations are in parentheses

(*a*) Molecule (A)

	x	*y*	*z*	*B*
Ni	470(1)	172(1)	1 221(1)	*
O(1)	646(6)	−995(6)	1 473(7)	*
O(2)	−756(6)	−180(6)	1 339(7)	*
N(1)	1 686(9)	493(8)	1 101(9)	*
N(2)	298(9)	1 331(8)	1 021(9)	*
C(1)	1 433(11)	−1 345(10,	1 517(11)	4.8(4)
C(2)	1 390(13)	−2 258(12)	1 700(13)	6.7(4)
C(3)	2 218(15)	−2 722(14)	1 804(14)	8.0(5)
C(4)	3 100(15)	−2 188(14)	1 689(15)	7.9(5)
C(5)	3 115(13)	−1 320(13)	1 485(13)	7.1(5)
C(6)	2 286(12)	−863(11)	1 413(12)	5.7(4)
C(7)	2 364(12)	9(12)	1 195(12)	6.1(4)
C(8)	1 847(15)	1 415(14)	792(15)	8.3(5)
C(9)	1 144(16)	1 916(16)	891(17)	9.6(6)
C(10)	−449(12)	1 702(11)	999(12)	5.9(4)
C(11)	−1 318(10)	1 237(10)	1 125(10)	4.6(3)
C(12)	−2 091(12)	1 735(12)	1 058(12)	6.1(4)
C(13)	−2 958(12)	1 311(12)	1 121(12)	6.1(4)
C(14)	−3 102(12)	392(11)	1 244(12)	5.6(4)
C(15)	−2 348(11)	−104(10)	1 303(11)	4.7(3)
C(16)	−1 452(10)	330(9)	1 257(10)	3.6(3)

* Anisotropic thermal parameters:

	B_{11}	B_{12}	B_{13}	B_{22}	B_{23}	B_{33}
Ni	48(1)	−4(2)	40(2)	40(1)	−4(2)	55(1)
O(1)	51(5)	21(8)	65(8)	46(5)	−8(9)	83(6)
O(2)	52(5)	12(8)	49(8)	35(5)	1(9)	76(6)
N(1)	81(8)	−20(12)	76(12)	36(7)	1(12)	88(8)
N(2)	62(7)	−33(12)	76(12)	43(7)	3(13)	103(9)

(*b*) Molecule (B)

	x	*y*	*z*	*B*
Ni	−411(1)	194(1)	3 760(1)	†
O(1)	658(6)	−224(6)	3 647(7)	†
O(2)	−1 026(7)	−947(7)	3 534(7)	†
N(1)	202(10)	1 328(9)	3 938(11)	†
N(2)	−1 504(10)	585(8)	3 866(10)	†
C(1)	1 529(10)	234(10)	3 710(10)	4.7(3)
C(2)	2 262(12)	−241(11)	3 656(12)	5.6(4)
C(3)	3 206(13)	212(12)	3 714(13)	6.8(5)
C(4)	3 416(14)	1 122(13)	3 829(14)	7.5(5)
C(5)	2 708(14)	1 578(13)	3 880(14)	7.5(5)
C(6)	1 732(12)	1 144(11)	3 830(11)	5.7(4)
C(7)	1 066(13)	1 646(12)	3 952(13)	6.6(4)
C(8)	−425(19)	1 962(18)	4 052(19)	11.4(7)
C(9)	−1 318(17)	1 494(16)	4 138(17)	10.0(6)
C(10)	−2 355(12)	141(11)	3 755(12)	6.0(4)
C(11)	−2 610(11)	−731(11)	3 580(11)	5.6(4)
C(12)	−3 617(13)	−1 135(12)	3 478(13)	6.5(4)
C(13)	−3 888(14)	−1 995(13)	3 321(14)	7.7(5)
C(14)	−3 251(14)	−2 555(13)	3 235(14)	7.7(5)
C(15)	−2 242(13)	−2 171(12)	3 356(13)	6.5(4)
C(16)	−1 943(11)	−1 259(10)	3 503(11)	4.7(3)

† Anisotropic thermal parameters:

	B_{11}	B_{12}	B_{13}	B_{22}	B_{23}	B_{33}
Ni	67(1)	28(2)	44(2)	45(1)	−9(2)	57(1)
O(1)	58(5)	0(8)	66(8)	41(5)	−18(9)	82(6)
O(2)	62(6)	6(9)	72(8)	52(6)	−9(9)	78(6)
N(1)	89(9)	47(13)	68(14)	54(8)	−11(15)	115(10)
N(2)	105(9)	50(12)	33(14)	39(7)	−18(12)	84(9)

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[14] M. Calligaris, G. Nardin, and L. Randaccio, *Co-ordination Chem. Rev.*, 1972, **7**, 385.

[15] L. M. Shkol'nikova, E. M. Yumal', E. A. Shugam, and V. A. Voblikova, *Zhur. strukt. Khim.*, 1970, **11**, 886.

TABLE 4

Fractional co-ordinates ($\times 10^4$) and thermal factors (Å) of $Na(BPh_4)\cdot4MeCN$ portion of complex (II). Anisotropic temperature factors ($\times 10^4$) are as in Table 1; estimated standard deviations are in parentheses

	x	*y*	*z*	*B*
Na	−286(4)	−1 366(4)	2 488(4)	*
B	5 473(12)	3 521(11)	2 376(12)	4.0(4)
C(17)	5 173(10)	2 905(10)	1 393(10)	4.2(3)
C(18)	4 671(11)	2 068(10)	1 324(11)	4.8(4)
C(19)	4 360(11)	1 553(11)	457(12)	5.5(4)
C(20)	4 538(12)	1 945(11)	−356(12)	5.7(4)
C(21)	5 012(12)	2 776(12)	−311(12)	6.0(4)
C(22)	5 337(12)	3 264(11)	548(12)	5.8(4)
C(23)	5 624(10)	2 980(10)	3 409(10)	4.4(3)
C(24)	6 045(11)	2 210(10)	3 648(11)	5.2(4)
C(25)	6 273(13)	1 794(13)	4 638(13)	6.8(5)
C(26)	6 041(13)	2 166(12)	5 327(13)	6.4(4)
C(27)	5 647(13)	2 934(12)	5 125(13)	6.4(4)
C(28)	5 421(12)	3 347(12)	4 183(12)	5.9(4)
C(29)	6 585(10)	4 111(10)	2 624(10)	4.4(3)
C(30)	6 839(12)	4 890(11)	3 134(12)	5.8(4)
C(31)	7 864(13)	5 336(12)	3 482(13)	6.8(5)
C(32)	8 589(13)	4 999(13)	3 277(14)	7.3(5)
C(33)	8 364(14)	4 219(14)	2 791(14)	7.9(5)
C(34)	7 340(12)	3 776(11)	2 457(12)	5.7(4)
C(35)	4 522(10)	4 087(10)	2 039(10)	4.3(3)
C(36)	3 603(11)	3 665(11)	2 094(11)	5.3(4)
C(37)	2 715(13)	4 093(12)	1 756(13)	6.7(4)
C(38)	2 742(13)	4 933(13)	1 341(13)	6.9(5)
C(39)	3 596(14)	5 379(13)	1 253(14)	7.3(5)
C(40)	4 520(12)	4 927(11)	1 621(12)	5.9(4)
N(5)	549(11)	−2 569(10)	3 562(11)	*
N(6)	−1 497(11)	−2 587(11)	1 500(11)	*
N(7)	−282(18)	3 951(17)	705(17)	14.2(8)
N(8)	1 371(19)	4 071(18)	3 678(19)	15.3(8)
C(41)	1 054(13)	−3 038(12)	4 072(13)	6.3(4)
C(42)	1 731(16)	−3 703(15)	4 717(16)	9.0(6)
C(43)	−2 100(12)	−3 144(12)	1 180(12)	5.9(4)
C(44)	−2 892(15)	−3 882(14)	782(15)	8.1(5)
C(45)	−184(19)	4 587(18)	1 100(19)	11.3(7)
C(46)	−71(20)	5 482(18)	1 492(20)	11.8(8)
C(47)	2 220(19)	4 206(17)	4 005(18)	11.1(7)
C(48)	3 324(22)	4 436(21)	4 420(22)	13.9(9)

* Anisotropic thermal parameters:

	B_{11}	B_{12}	B_{13}	B_{22}	B_{23}	B_{33}
Na	64(3)	15(5)	65(5)	44(3)	2(5)	74(3)
N(5)	118(11)	86(15)	61(16)	90(10)	19(16)	89(10)
N(6)	115(11)	−28(17)	106(16)	80(10)	−10(17)	110(10)

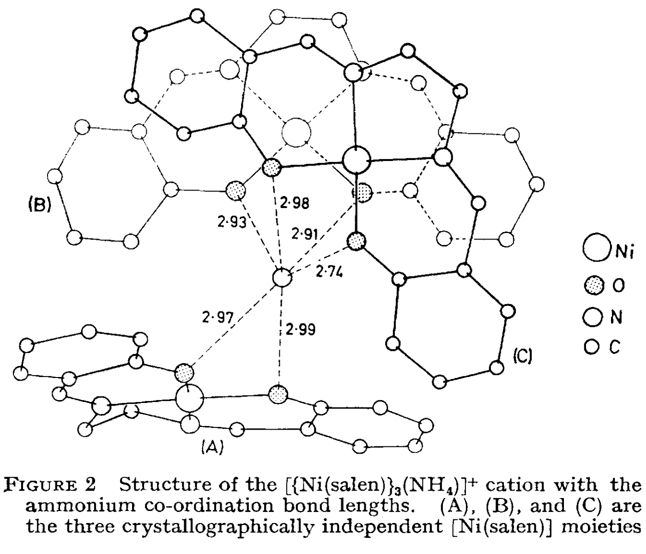

FIGURE 2 Structure of the $[\{Ni(salen)\}_3(NH_4)]^+$ cation with the ammonium co-ordination bond lengths. (A), (B), and (C) are the three crystallographically independent [Ni(salen)] moieties

TABLE 5

Weighted average values of bond lengths (Å) and angles (°) with their standard deviation in parentheses; M′ represents $[NH_4]^+$ in complex (I) and Na^+ in (II)

	(I)	(II)
(*a*) Distances		
Ni–O	1.87(1)	1.860(3)
Ni–N	1.92(1)	1.848(5)
O–C(1)	1.31(3)	1.336(4)
N–C(7)	1.29(3)	1.288(4)
N–C(8)	1.55(2)	1.483(10)
C(1)–C(2)	1.43(2)	1.419(5)
C(1)–C(6)	1.52(1)	1.410(3)
C(2)–C(3)	1.41(2)	1.432(10)
C(3)–C(4)	1.39(2)	1.432(17)
C(4)–C(5)	1.36(4)	1.363(6)
C(5)–C(6)	1.41(4)	1.454(8)
C(6)–C(7)	1.41(4)	1.396(18)
C(8)–C(9)	1.44(4)	1.444(3)
B–C	1.64(4)	1.655(10)
C–C(Ph)	1.45(1)	1.419(7)
M′–O	2.92(4)	2.407(7)
M′–N		2.488(8)
(*b*) Angles		
O(1)–Ni–O(2)	85(1)	84.44(5)
O(1)–Ni–N(1)	92.6(6)	94.3(1)
O(1)–Ni–N(2)	176.0(6)	178.2(2)
N(1)–Ni–N(2)	88(1)	86.9(3)
Ni–O–C(1)	127(2)	126.6(3)
Ni–N–C(7)	128(1)	128.2(3)
Ni–N–C(8)	108(2)	114.4(3)
C(7)–N–C(8)	122(2)	117.2(5)
O–C(1)–C(2)	119(1)	116.1(2)
O–C(1)–C(6)	124(2)	123.3(3)
N–C(7)–C(6)	126(2)	124.1(5)
N–C(8)–C(9)	109(2)	111.1(7)
C(1)–C(2)–C(3)	122(2)	119.8(6)
C(1)–C(6)–C(5)	119(2)	118.9(4)
C(1)–C(6)–C(7)	119(2)	123.3(2)
C(2)–C(3)–C(4)	120(3)	118.4(11)
C(4)–C(5)–C(6)	121.0(6)	121.4(6)
C(5)–C(6)–C(7)	122(1)	117.7(4)
C–B–C(Ph)	110(1)	109(2)
C–C–C(Ph)	120(1)	119.8(4)
B–C–C(Ph)	122(2)	121.0(7)
O–M′–O(2)	51.7(9)	62.6(4)
Ni–O–M′	102(1)	99.2(1)

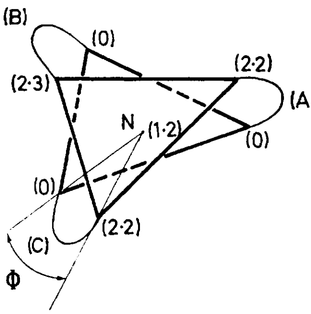

FIGURE 3 A sketch of the $[NH_4]^+$, (N), co-ordination polyhedron. Numbers in parentheses are relative displacements (Å) of the atoms from the basal triangular face

within ±0.06 Å. The [Ni(salen)] portions show slight deviations from planarity. Their conformation may be described [14] as 'stepped' for the (B) and (C) molecules and 'umbrella shaped' for the (A) molecule. The ethylene bridges have a nearly *gauche* conformation, with torsion angles of 35, 42, and 41° for molecules (A), (B), and (C).

Bond lengths and angles in the tetraphenylborate anion are in the usual ranges, as are also the interplanar angles (60—79°) between each pair of phenyl rings.[9,16]

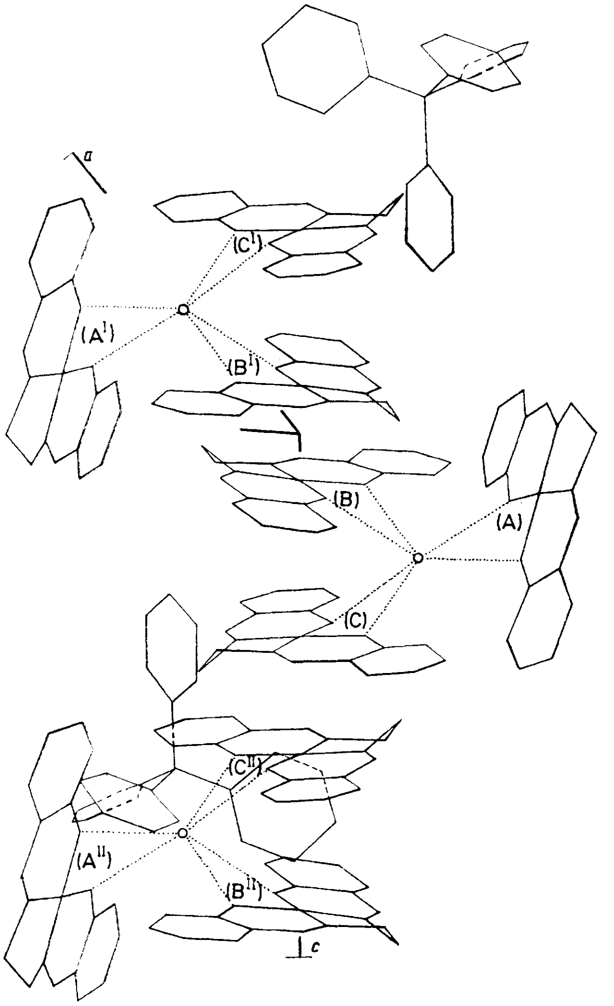

FIGURE 4 Part of the cell contents projected so to avoid too much overlapping of atoms. (A), (B), and (C) are as for Figure 2. Roman numerals refer to the following equivalent positions relative to the molecules at x, y, z: I, $\bar{x}, \bar{y}, \bar{z}$; II, $\bar{x}, \bar{y}, 1 - \bar{z}$

The crystal packing is shown in Figure 4 where only part of the cell contents is projected for the sake of clarity. It may be seen that the closest contacts occur along the crystallographic c axis, so that the centrosymmetric [Ni(salen)] molecules, like (B), (B^{I}) and (C), (C^{II}), are coupled in a manner similar to that found in the packing of [Ni(salen)] itself.[15] In the latter structure, however, the Ni $\cdots$ Ni distance is 3.21(1) Å whereas in (I) it is longer, mean 3.50(1) Å. There are few contacts involving the (A) and thf molecules or $[BPh_4]^-$. This addition compound may therefore be considered, at least in the solid state, as being a ' complex ' rather than a simple lattice compound because of the absence of direct contacts between oppositely charged ions. Thus the crystal structure may be described in terms of $[\{Ni(salen)\}_3(NH_4)]^+$ macrocations and $[BPh_4]^-$ anions with thf molecules in the resulting voids. These are however very loosely bound in the crystal as shown by the severe disorder found.

Complex (II).—The crystal consists of discrete cations $[\{Ni(salen)\}_2Na(NCMe)_2]^+$ and anions $[BPh_4]^-$ with four acetonitrile molecules of crystallization per unit cell. The macrocation (Figure 5), is very similar to the cobalt analogue,[4,9] $[\{Co(salen)\}_2Na(thf)_2]^+$, except for the difference in co-ordinated solvent. The sodium ion is surrounded by four oxygen atoms of the [Ni(salen)] units and by the nitrogen atoms of two *cis*-acetonitrile molecules in an environment which approximates to an octahedral polyhedron, similar to those found in both the cobalt– and copper–sodium derivatives.[8,9] The ligands are arranged so as to confer approximately C_2 symmetry on the whole cation, the two-fold axis passing through sodium and the midpoint of the nickel atoms.

The $Na^+ \cdots O$ distances [2.39—2.42(1) Å] are similar to those found previously,[8,9] as is the geometry of the salen ligand.[14] The Ni-O distances range from 1.858(9) to 1.870(10) Å; the mean [1.860(3) Å] appears slightly longer than that of the parent complex [Ni(salen)] [1.83(1) Å],[15] and is closer to that for the addition complex between [Ni(salen)] and $SnMe_2Cl_2$ [1.86(1) Å].[2]

The co-ordinated acetonitrile molecules are almost linear and approximately aligned with Na^+, the N–C–C and Na–N–C angles being 177(1) and 169(1)°. No difference is found between co-ordinated and non-co-ordinated solvent molecules [means: N–C 1.126(6), C–C 1.495(16) Å].

The stereochemistry of the nickel atoms is essentially square planar, the maximum out-of-plane displacement in the NiO_2N_2 group being ± 0.02 Å. The [Ni(salen)] molecules themselves are nearly planar, the dihedral angles between the salicylaldimine residues not exceeding 3°. The torsion angles around the C(8)–C(9) bond of the ethylene bridges are 14 and 15° respectively for molecules (A) and (B) and corresponding C–C bond lengths are 1.44 and 1.45(4) Å. It is a general feature of salen complexes that small deviations of the ethylene bridge carbon atoms from the M–N–N plane occur together with a shortening of the C–C distances.[15] It seems likely that such short values are not real, but

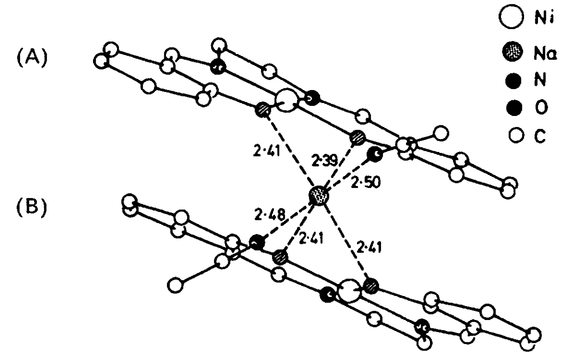

FIGURE 5 Structure of the $[\{Ni(salen)\}_2Na(NCMe)_2]^+$ cation with the sodium co-ordination bond lengths. (A) and (B) are two crystallographically independent [Ni(salen)] moieties

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[16] M. di Vaira and A. Bianchi Orlandini, *J.C.S. Dalton*, 1972, 1704.

attributable to the thermal motion in the crystals. On the other hand, correction for internal motions are often inadequate.[7]

The geometry of the tetraphenylborate anion is similar to that found in complex (I), the boron atom being nearly tetrahedral and the interplanar angles between pairs of phenyl rings ranging from 52 to 90°.

Environment of Co-ordinated Cations.—Since alkali or alkaline-earth cations M′ can be described as being positively charged spheres which interact electrostatically with negative charges without particular restrictions in bond directions, different co-ordination environments around M′ are possible, depending on the nature of the ligand and the ionic radius of M′.[5,7] In the case of [M(salen)] molecules as neutral ligands there is far less flexibility than in organic systems and the co-ordination number found for Na^+, K^+, and $[NH_4]^+$ is generally six, even if values as low as four are probable for smaller cations such as Li^+.

In the 3 : 1 complexes of K^+ and $[NH_4]^+$, which may be considered as tris(chelate) complexes, the arrangement of the oxygen atoms is found to be intermediate between that of a trigonal prism and that of an octahedron. In fact the relative rotation angle, ϕ, of the opposite triangular faces (see Figure 3) is 26° while it would be 0 and 60° respectively for the two limiting geometries. The resulting polyhedron seems to be derived from a balance between electrostatic and steric factors, both of which are conditioned by the O · · · O bite of the chelating ligands. This, in turn, is determined by the co-ordination bond lengths and angles and is almost the same (mean 2.55 Å) for salen derivatives of Co, Ni, and Cu.[14] The important role of the bite values in determining the geometry of tris(chelate) complexes of transition metals has already been shown by Kepert.[17] He has analyzed the influence of the bite on the stereochemistry of tris(bidentate) complexes on the basis of the total ligand–ligand repulsion energy.[17] His results show that for a ' normalized bite ' (O–O/M′–O) of *ca.* 0.9, as in the present case, the octahedral stereochemistry is far less stable than is the prismatic. On the other hand, prismatic geometry would not allow the favourable interactions among the [M(salen)] units which are present in the distorted polyhedron. In fact in all the complexes containing dimeric species, the [M(salen)] molecules are never perfectly ' faced ' as would be implied by $\phi = 0$.

However, Kepert's model seems to be oversimplified for the correct prediction of the stereochemistry of tris(bidentate chelate) complexes. In fact, in transition-metal complexes it neglects the directional properties of the metal–ligand bonds, while in alkali-ion complexes it does not take into account electrostatic interactions with the central cation. Trigonal-prismatic geometry has been found in sodium compounds containing chelating ligands such as 1,1,1-trifluoropentane-2,4-dionate and 1,2-bis(diphenylphosphino)methane,[18,19] in contrast to the value of 1.2 found for the ' normalized bite ' which should give a ϕ angle of *ca.* 40°.

In any case the structure of the latter complexes supports the conclusion that the octahedral environment of the co-ordinated cation seems to be unfavourable. On the other hand in the 2 : 1 complexes the lack of restraints due to the presence of a third bulky chelating ligand makes it possible for polyhedra to be closer to the octahedron. In fact the approximate values of ϕ in the copper–, cobalt–, and nickel–salen 2 : 1 sodium derivatives are *ca.* 40°.[8,9] This seems to be in agreement with the predictions of Kepert's model for six-co-ordinate $[M(bidentate)_2(unidentate)_2]$ complexes when the ' normalized bite ' is *ca.* 1.0.[20] In fact, in this case, the *cis*-octahedral structure is the most stable, the energy increasing for the following idealized structures: *cis*-octahedral < trigonal prismatic < distorted pentagonal pyramid < *trans*-octahedral.

Octahedral arrangements are to be expected for six-co-ordinate cations in the case of unidentate ligands, such as acetone or thiocyanate ions.[21,22] However, steric effects can produce significant distortions from octahedral geometry just as in the case of the sodium–dimethylformamide complex.[23] A non-bonded interaction-energy calculation [24] shows that the octahedral geometry is highly destabilized if $P\bar{6}2c$ crystallographic symmetry is maintained.

In the [M(salen)]–alkali-metal complex the [M(salen)] molecules are arranged so as to stabilize the macrocations through formation of attractive van der Waals contacts. However, in the case of very small cations such as Li^+ the reduction in M′ · · · O distance would imply too close contacts between the chelate molecules and which could explain the 1 : 1 molar ratio found in [M(salen)]–Li derivatives,[4] in which a tetrahedral environment of the alkali ion is to be expected.

At present it is difficult to assess the influence of the co-ordinated cations on the M–O co-ordination distances in view of the few accurate data available. However, in the sodium complex (II) the Ni–O distances [1.86—1.87(1) Å] appear to be slightly longer (3σ) than those of [Ni(salen)] [1.83(1) Å].[15] This lengthening, if really significant, would reflect a partial draining of charge from the transition-metal atom, just as is generally observed when the Schiff-base oxygen atoms undergo further co-ordination.[14] However, this effect does not appear in the other sodium complexes [8,9] suggesting that the influence of the alkali ion is not reflected in the co-ordination bond lengths.

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[5/2307 *Received, 25th November*, 1975]

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[17] D. L. Kepert, *Inorg. Chem.*, 1972, **11**, 1561.

[18] D. E. Fenton, C. Nave, and M. R. Truter, *J.C.S. Dalton*, 1973, 2188.

[19] W. Hewertson, B. T. Kilbourn, and R. H. B. Mais, *Chem. Comm.*, 1970, 952.

[20] D. L. Kepert, *Inorg. Chem.*, 1973, **12**, 1944.

[21] P. Piret, Y. Gobillon, and M. van Meerssche, *Bull. Soc. chim. France*, 1963, 205.

[22] P. H. van Rooyen and J. C. A. Boeyens, *Acta Cryst.*, 1975, **B31**, 2933.

[23] Y. Gobillon, P. Piret, and M. van Meerssche, *Bull. Soc. chim. France*, 1962, 551.

[24] M. Calligaris, unpublished work.