Alkali-metal Salt Adducts of Nickel(II) Complexes of Quadridentate Schiff-base Ligands. The *X*-Ray Structure of *NN*′-Ethylenebis(acetylacetoneiminato)nickel(II)

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Adducts of sodium perchlorate, sodium thiocyanate, and lithium perchlorate with *NN*′-ethylenebis(salicylideneiminato)- and *NN*′-ethylenebis(acetylacetoneiminato)-nickel(II) are reported. All have alkali-metal ion: nickel complex ratios of 1 : 2. The title complex crystallizes in the space group *C*2/*c* with a = 19.728(4), b = 10.832(2), c = 15.012(3) Å, β = 112.85(8)°, and Z = 4. The *X*-ray structure determination (heavy-atom method, 2 549 unique reflections measured by a four-circle diffractometer, *R* 0.04) has shown that the Na^+ ion lies on a crystallographic two-fold axis with an irregular six-fold co-ordination sphere defined by oxygen atoms from two nickel complexes and a disordered perchlorate anion.

THE Schiff-base ligand *NN*′-ethylenebis(salicylideneiminate) (salen) yields transition-metal complexes (1) which may be further co-ordinated through the *cis*-oxygen atoms to other metal ions such that new bi- and tri-nuclear metal complexes are produced.[1] For example, (1; M = Cu) reacts with a range of bivalent transition-metal ions to form complexes of types [Cu(salen)]·MX_2 and 2[Cu(salen)]·MX_2 (X = anion).[2-4] Studies of the magnetic and spectral properties [3-5] have been of particular interest for many such complexes because of the close proximity [6] of the transition-metal ions. A few adducts of this type formed by non-transition-metal ions have also been reported [3] and *X*-ray structure determinations of 2[Cu(salen)]·Na[ClO_4]·C_8H_{10},[7] [Co(salen)]·Na[BPh_4]·2thf (thf = tetrahydrofuran),[8a] and 2[Ni(salen)]·[Na$(NCMe)_2$][BPh_4]·2MeCN [8b] have revealed a co-ordination number of six for the sodium ions in each case.

Recently it has been demonstrated that *NN*′-ethylenebis(acetylacetoneiminato)nickel(II), [Ni(acen)] (2; M = Ni), reacts in deuteriochloroform with lanthanoid shift

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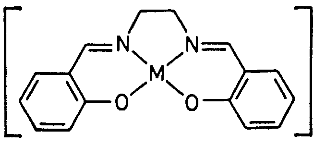
reagents such as [Eu(fod)$_3$] (fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionate) to yield 1 : 1 adducts.[9] Although square-planar complexes (2) appear



[M(salen)]

(1)

to co-ordinate to a second metal ion less readily than the corresponding derivatives (1),[1] a few adducts of (2; M = Cu) with metal ions as well as with quaternary ammonium cations [10] have been isolated.

TABLE 1

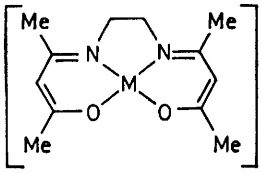
Infrared and analytical data

Complex	Selected i.r. absorptions (cm^{-1})		Analysis (%)							
			Found				Calc.			
	γ(C–O)	Anion	C	H	N	Ni	C	H	N	Ni
2[Ni(salen)]·Na[ClO$_4$]·H$_2$O	1 550 (sh), 1 540	1 090	48.85	4.00	7.25	15.0	48.6	3.80	7.10	14.9
2[Ni(salen)]·Na[NCS]·CHCl$_3$	1 550, 1 540 (sh)	2 070	48.55	3.60	8.35	14.1	48.5	3.45	8.30	13.9
2[Ni(salen)]·Li[ClO$_4$]	1 550, 1 540 (sh)	1 090	50.6	3.95	7.75	15.2	50.8	3.75	7.40	15.5
2[Ni(acen)]·Na[ClO$_4$]		1 110, 1 070	42.3	5.60	8.60	17.2	42.1	5.30	8.20	17.2
2[Ni(acen)]·Na[NCS]		2 065	46.85	5.90	10.6	18.4	46.7	5.65	10.9	18.3
2[Ni(acen)]·Li[ClO$_4$]·H$_2$O		1 120, 1 070	42.0	5.90	8.15	17.2	42.0	5.60	8.15	17.1

We now report new examples of alkali-metal adduct formation by nickel complexes of types (1) and (2). An *X*-ray structural investigation of the sodium perchlorate adduct of [Ni(acen)] is also described.

EXPERIMENTAL

The complexes were prepared by a procedure related to that reported previously.[3] The nickel complex was dissolved in a minimum amount of dry chloroform to which



[M(acen)]

(2)

was added the metal salt in a minimum amount of absolute ethanol. The crystalline adduct in most cases precipitated on evaporation of the solution. In some cases addition of small amounts of diethyl ether was necessary to induce crystallization. Selected products were purified by recrystallization from dry methanol–acetone. The adducts were washed with diethyl ether and dried *in vacuo* over P$_4$O$_{10}$ before analysis.

Analyses for C, H, and N (Table 1) were by the Australian Microanalytical Service, Melbourne. Infrared spectra were obtained on a Jasco IRA-1 spectrophotometer using paraffin mulls, n.m.r. spectra on a Jeol JNM-MH-100 spectrometer.

X-Ray Crystallography.—Crystal data for 2[Ni(acen)]·Na[ClO$_4$]. $M = 684.5$, Monoclinic, $a = 19.728(4)$, $b = 10.832(2)$, $c = 15.012(3)$ Å, $\beta = 112.85(7)°$, $U = 2\,956$ Å^3, $D_m = 1.55$ g cm^{-3}, $Z = 4$, $D_c = 1.538$ g cm^{-3}, Mo-K_α radiation, $\lambda = 0.710\,7$ Å, μ(Mo-K_α) = 14.3 cm^{-1}, $F(000) = 1\,424$, space group $C2/c$.

Data were collected on a crystal with dimensions *ca.* 0.12 × 0.11 × 0.08 mm using a Philips PW1100 four-circle diffractometer and graphite-monochromatized Mo-K_α radiation. A θ—2θ scan mode was used and reflections with $3.0 < \theta < 32°$ in one quadrant were examined. Weak reflections which gave $I_t - 2(I_t)^{\frac{1}{2}} < I_b$ on the first scan were not further examined (I_t = the intensity at the top of the reflection peak and I_b = the mean of two preliminary 5-s background measurements on either side of the peak). Of the remaining reflections, those for which the total intensity recorded in the first scan of the peak (I_i) was <500 counts were scanned twice to increase their accuracy. A constant scan speed of 0.05° s^{-1} and a variable scan width of $(0.7 + 0.1 \tan \theta)°$ were used, with a background measuring time proportional to I_b/I_i. Three standard reflections were measured every 6 h during data collection and showed no significant variations in intensity.

The reflection intensities were calculated from the peak and background measurements using a program written for the PW1100 diffractometer.[11] The variance of the intensity, I, was calculated as the sum of the variance due to counting statistics and $(0.04I)^2$, where the term in I^2 was introduced to allow for other sources of error.[12] I and $\sigma(I)$ were corrected for Lorentz and polarization factors and 2 549 reflections having $I > 3\sigma(I)$ were found to be statistically significant. No absorption corrections were applied.

Structure solution and refinement. The chlorine and two nickel atoms were located from a Patterson map. Least-

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squares refinement of their positional and isotropic thermal parameters gave R 0.34. A subsequent difference-Fourier synthesis revealed the position of the sodium ion and all the non-hydrogen atoms of the [Ni(acen)] complex, but gave a complex pattern of electron-density maxima about the chlorine atom. The chlorine and the sodium atoms lie in special positions (on a two-fold axis), as required by the centrosymmetric space group $C2/c$ with $Z = 4$. Refinement with isotropic parameters for all the atoms converged at R 0.13, and at this stage difference-Fourier maps confirmed disorder of the perchlorate oxygen atoms. No simple model for this disorder could be derived from the positions of the electron-density maxima. Assigning the six most intense independent maxima as oxygen atoms and refining their population parameters revealed the major orientation of the $[ClO_4]^-$ group as defined by the oxygen atoms O(17) and O(18) (population parameters 0.54 and 0.45) and O(17′) and O(18′) related by the two-fold axis. The remaining atoms O(19)—O(22) had lower populations in the range 0.13—0.27 and did not define physically reasonable O–Cl–O angles. Population parameters were fixed (Table 2) so that the total number of electrons surrounding the Cl atom was equivalent to four oxygen atoms.

In the final cycles of full-matrix least-squares refinement all the atoms except O(19)—O(22) were assigned anisotropic thermal parameters and hydrogen atoms were included in calculated positions (C–H 1.08 Å), but not refined, with isotropic thermal parameters 20% greater than those of the attached carbon atoms. This resulted in R 0.040 and R' 0.051, where $R' = \Sigma||F_o| - |F_c||w^{\frac{1}{2}}/\Sigma|F_o|w^{\frac{1}{2}}$ and weights (w) were assigned to reflections as $w = 1/\sigma^2(F_o)$, (maximum shift/σ) = 0.60, and (average shift/σ) = 0.061. The final difference-Fourier map showed maxima and minima of electron density of 0.19 and -0.15 eÅ^{-3}, respectively.

TABLE 2

Refined atomic positional parameters (× 10^4)

Atom	x/a	y/b	z/c
Ni	3 243.0(2) [a]	1 557.4(4)	1 685.3(3)
Na	5 000	2 351(2)	2 500
Cl(1)	5 000	5 457(2)	2 500
O(1)	4 088(1)	960(2)	1 570(2)
C(2)	4 114(2)	148(4)	950(3)
C(3)	3 516(2)	−240(4)	172(3)
C(4)	2 785(2)	164(4)	−50(3)
N(5)	2 606(1)	862(3)	536(2)
C(6)	1 840(2)	1 279(4)	240(3)
C(7)	1 720(2)	1 718(4)	1 104(4)
N(8)	2 420(1)	2 166(3)	1 839(2)
C(9)	2 410(2)	2 848(4)	2 551(3)
C(10)	3 059(2)	3 216(3)	3 324(3)
C(11)	3 757(2)	2 909(3)	3 436(3)
O(12)	3 914(1)	2 251(2)	2 821(2)
C(13)	4 870(2)	−364(4)	1 156(3)
C(14)	2 202(2)	−276(5)	−1 002(3)
C(15)	1 690(2)	3 310(4)	2 561(4)
C(16)	4 416(2)	3 337(4)	4 303(3)
O(17) [b]	4 531(4)	4 535(10)	1 731(6)
O(18) [b]	5 371(8)	6 131(10)	2 101(12)
O(19) [b]	4 464(13)	6 461(22)	3 214(18)
O(20) [b]	4 690(17)	5 891(28)	1 579(19)
O(21) [b]	5 612(9)	5 662(14)	2 145(12)
O(22) [b]	4 648(8)	4 386(16)	2 150(10)

[a] Estimated standard deviations are given in parentheses in this and subsequent tables. [b] Population parameters: O(17) and O(18), 0.5; O(19) and O(20), 0.2; O(21) and O(22), 0.3.

Major computations were made using the 'X-RAY' system of programs.[13] Scattering factors were taken from ref. 14 (ref. 15 for H atoms) and included both real and imaginary contributions to anomalous scattering for the Na, Cl, and Ni atoms.[16] The refined atomic positional parameters are presented in Table 2, bond lengths and angles in Table 3 and Figure 2. Atomic thermal parameters, intermolecular contacts, equations of least-squares planes, and observed and calculated structure factors are to be found in Supplementary Publication No. SUP 22083 (16 pp.).*

TABLE 3

Interatomic distances (Å) and angles (°) in the $Na[ClO_4]$ moiety

Na–O(1)	2.346(3)	O(12)–Na–O(12^{I})	174.8(2)
Na–O(12)	2.374(3)	O(12)–Na–O(17^{I})	98.2(2)
Na–O(17)	2.638(10)	O(17)–Na–O(17^{I})	52.5(3)
Cl–O(17)	1.54(1)	O(17)–Cl–O(18)	107.1(7)
Cl–O(18)	1.33(2)	O(17)–Cl–O(17^{I})	98.9(5)
O(1)–Na–O(12)	63.1(1)	O(17)–Cl–O(18^{I})	114.8(6)
O(1)–Na–O(17)	105.0(3)	O(18)–Cl–O(18^{I})	113.3(8)
O(1)–Na–O(1^{I})	100.1(1)	Ni–O(1)–Na	103.3(1)
O(1)–Na–O(12^{I})	113.2(1)	Ni–O(1)–C(2)	126.2(2)
O(1)–Na–O(17^{I})	153.4(2)	Ni–O(12)–Na	102.1(1)
O(12)–Na–O(17)	86.5(3)	Ni–O(12)–C(11)	126.3(2)

The superscript I corresponds to the equivalent position $1 - x, y, \frac{1}{2} - z$ relative to an atom at x, y, z in Table 2.

RESULTS AND DISCUSSION

The adducts prepared (Table 1) all show a metal complex to alkali metal ratio of 2 : 1. The complexes of salen are thus formally analogous to the previously reported adducts derived from [Cu(salen)].[1,3,7] Adduct formation by [Ni(salen)] or [Ni(acen)] does not result in significant change in the respective visible-reflectance spectra but i.r. spectra can be used diagnostically to show that complex formation has occurred. The appearance of perchlorate or thiocyanate bands is very evident, but a change in the phenolic C–O stretching mode in the 1 500—1 600 cm^{-1} region can also be used to indicate adduct formation for complexes of salen. The band at 1 536 cm^{-1} of [Ni(salen)] has been assigned previously to the C–O bond stretch [17] and the frequency of this absorption is expected to increase on adduct formation.[4] For the present adducts (Table 1) there is a consistent increase in the frequency of this absorption over the position in free [Ni(salen)]; this shift to higher energy is compatible with increasing constraint in the C–O bond arising from bridge formation by each oxygen. A similar trend appears to occur for the adducts of [Ni(acen)]; however, for these the spectra are considerably more complex in this region and definite assignments are difficult.

The n.m.r. spectra of the [Ni(acen)] adducts were

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

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measured in deuteriochloroform and compared with that of [Ni(acen)].[9,18] Only very small shifts in the various resonances were observed (all less than 0.05 p.p.m.); this parallels previously reported results.[19]

The nature of the interaction between Na[ClO$_4$] and [Ni(acen)] was examined in solid 2[Ni(acen)]·Na[ClO$_4$] by *X*-ray crystallography. This adduct crystallizes in the space group $C2/c$ with $Z = 4$, which requires the formula unit to have crystallographic symmetry. The sodium and chlorine atoms are located on a two-fold axis as shown in Figure 1. There is no evidence from intermolecular contacts for association between formula units in the solid state.

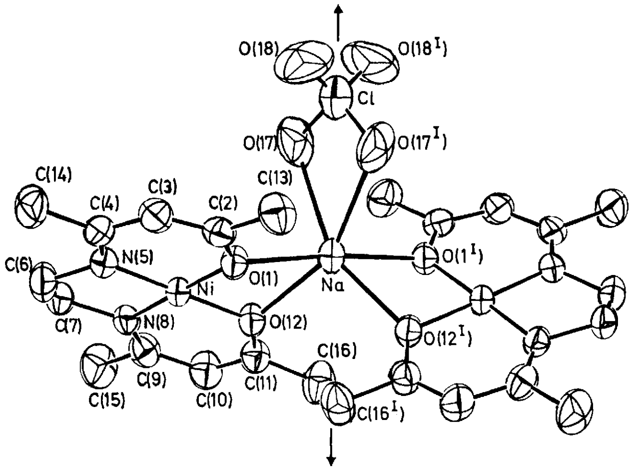

FIGURE 1 The 2[Ni(acen)]·Na[ClO$_4$] unit showing the atom-labelling scheme used in Table 2. The superscript I corresponds to the equivalent position $1 - x, y, \frac{1}{2} - z$ relative to an atom at x, y, z in Table 2. The arrows indicate the two-fold crystallographic axis

The perchlorate ion is significantly disordered, and only the principal sites of oxygen atoms are illustrated in Figure 1. For this orientation of the oxygen atoms the O–Cl–O angles show significant deviations from those expected for a tetrahedral ion (Table 3), but these values are probably a consequence of the inadequacies of the model for the disorder rather than distortions caused by interactions with the Na$^+$ ion. A second data set for another crystal of 2[Ni(acen)]·Na[ClO$_4$] gave no better definition of the perchlorate oxygen atoms. The disorder of the [ClO$_4$]$^-$ ion relative to the Na$^+$ is consistent with the formulation of these ions as an ion pair[7] as in the related structure 2[Cu(salen)]·Na[ClO$_4$]·C$_8$H$_{10}$. The Na . . . Cl distance (3.36 Å) is slightly larger than that (3.17 Å) in the [Cu(salen)] adduct[7] and the minimum Na . . . Cl distance (3.25 Å) in solid Na[ClO$_4$].[20]

The oxygen atoms from the [Ni(acen)] units related by the two-fold axis (see Figure 1) approach the Na$^+$ ion more closely than the perchlorate oxygen atoms, and complete the co-ordination sphere. Thus, with the main orientation of the [ClO$_4$]$^-$ as in Figure 1, the Na$^+$ has a co-ordination number of six. The co-ordination polyhedron is very irregular (Table 3). The O–Na–O angles defined by the chelating ligands [ClO$_4$]$^-$ and [Ni(acen)] are 52.5 and 63.1°.

The [Ni(acen)] unit is nearly planar. There is close agreement between bond lengths and angles in the two chemically equivalent halves of the [Ni(acen)] complex (see Figure 2), and the values are similar to those reported for [Cu(acen)][21,22] and [Ni(acen)][23] complexes except that the co-ordinate bonds to nickel are slightly shorter. The displacement of the Na$^+$ from the plane of the [Ni(acen)] complex and the angles subtended at the O(1) and O(12) atoms provide no evidence for alignment of lone pairs of electrons on these oxygen atoms with the Na–O axes.

The solid-state structure of 2[Ni(acen)]·Na[ClO$_4$] thus closely resembles that of 2[Cu(salen)]·Na[ClO$_4$]·C$_8$H$_{10}$ which also crystallizes in the space group $C2/c$ with the Na$^+$ and [ClO$_4$]$^-$ ions located on a two-fold axis. Methylammonium perchlorate forms[10,22] a 1 : 1 adduct with [Cu(acen)], which has been described as a lattice compound of complex molecules, methylammonium and perchlorate ions.[22] In contrast to the adduct 2[Ni(acen)]·Na[ClO$_4$], hydrogen bonding plays an important role in stabilizing the lattice.[22]

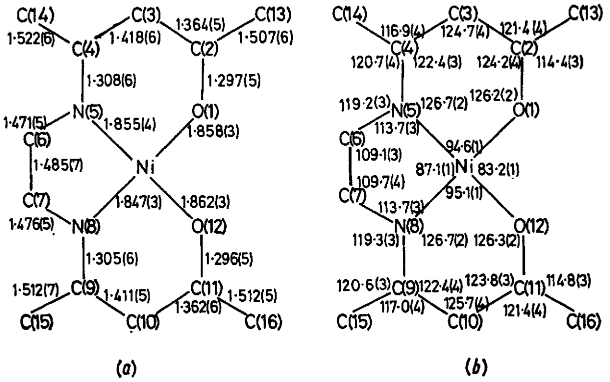

FIGURE 2 Bond lengths (*a*) and angles (*b*) in the [Ni(acen)] moiety

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