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Adduct Formation between Alkali Metal Ions and Divalent Metal Salicylaldimine Complexes Having Methoxy Substituents. A Structural Investigation

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Sodium, potassium, and cesium salts (iodides, nitrates, acetates, and tetraphenylborates) form 1/1, 1/2 and 2/3 adducts with ML_n [$M = Co$, Ni, Cu, and Zn; $n = 1-4$; $H_2L_1 = N,N'$-(3-methoxysalicylidene)ethane-1,2-diamine; H_2L_2, H_2L_3, and H_2L_4 are the -propane-1,2-diamine, -*o*-phenylenediamine, and -propane-1,3-diamine analogues of H_2L_1). Metal salicylaldimine, alkali metal, and anion all exert influence on stoichiometry and reactivity. Sodium ions tend to reside within the planes of the salicylaldimine oxygens, as in $Na(NO_3)(MeOH)\cdot NiL_4$ (**1**), $Na(NO_3)(MeOH)\cdot CuL_1$ (**2**; both with unusual seven-coordinated sodium), and $Na\cdot(NiL_4)_2I\cdot EtOH\cdot H_2O$ (**3**; with dodecahedral sodium coordination geometry). Potassium and cesium tend to locate between salicylaldimine ligands as in $KI\cdot NiL_4$ (**4**) and $[Cs(NO_3)\cdot NiL_4]_3\cdot MeOH$ (**5**; structures with infinite sandwich assemblies), $CsI\cdot(NiL_2)_2\cdot H_2O$ (**6**), $CsI_3\cdot(NiL_4)_2$ (**7**; simple sandwich structures), and $[K(MeCN)]_2\cdot(NiL_4)_3$ (**8**; a triple-decker sandwich structure). Crystal data for **1** are the following: triclinic, $P1$, $a = 7.3554(6)$ Å, $b = 11.2778(10)$ Å, $c = 13.562(2)$ Å, $\alpha = 96.364(10)°$, $\beta = 101.924(9)°$, $\gamma = 96.809(10)°$, $Z = 2$. For **2**, triclinic, $P1$, $a = 7.2247(7)$ Å, $b = 11.0427(6)$ Å, $c = 13.5610(12)$ Å, $\alpha = 94.804(5)°$, $\beta = 98.669(7)°$, $\gamma = 99.26(6)°$, $Z = 2$. For **3**, orthorhombic, $Pbca$, $a = 14.4648(19)$ Å, $b = 20.968(3)$ Å, $c = 28.404(3)$ Å, $Z = 8$. For **4**, triclinic, $P1$, $a = 12.4904(17)$ Å, $b = 13.9363(13)$ Å, $c = 14.1060(12)$ Å, $\alpha = 61.033(7)°$, $\beta = 89.567(9)°$, $\gamma = 71.579(10)°$, $Z = 2$. For **5**, monoclinic. $P2_1/n$, $a = 12.5910(2)$ Å, $b = 23.4880(2)$ Å, $c = 22.6660(2)$ Å, $\beta = 99.3500(1)°$, $Z = 4$. For **6**, orthorhombic, $Pbca$, $a = 15.752(3)$ Å, $b = 23.276(8)$ Å, $c = 25.206(6)$ Å, $Z = 8$. For **7**, triclinic, $P1$, $a = 9.6809(11)$ Å, $b = 10.0015(13)$ Å, $c = 11.2686(13)$ Å, $\alpha = 101.03°$, $\beta = 90.97°$, $\gamma = 100.55°$, $Z = 2$. For **8**, monoclinic, $C2/c$, $a = 29.573(5)$ Å, $b = 18.047(3)$ Å, $c = 23.184(3)$ Å, $\beta = 122.860(10)°$, $Z = 8$.

Introduction

Over these past 2 decades there has been enormous interest in the coordination chemistry of alkali metal ions, much of this interest originating from a desire to develop molecular systems that can mimic naturally occurring molecules responsible for the selective transport of ions. Structure/selectivity studies have focused strongly on crown ethers, cryptands, and related ligands. Although these are particularly good classes of complexing agents for alkali metal ions, there are many other simpler and certainly more affordable ligands that are also extremely effective in this respect. Metal salicylaldimines represent a fascinating group of ligands that are not only effective complexing agents for p- and d-block elements but also for alkali metal ions. Furthermore, some of the bimetallic systems resulting from alkali metal complexation have particularly important properties. The structures of a number of lithium, sodium, and potassium adducts of metal salicylaldimines have been determined,[1] as well as structures of sodium salts of the free ligands.[2] In some instances these adducts are precursors for other interesting molecular species concerning small molecule activation,[3] electron storage,[4−7] and the carrying of polar organometallics[8] or have remarkable magnetic properties (the alkali cation being crucial in determining the three-dimensional network in the solid state[9]). In fact, an analogous adduct of $Na\cdot(NiL_4)_2I$ (see Figure 1 for nomenclature), which is described in the present paper, has been indicated as the key intermediate compound in electron-transfer reactions between two metal salicylaldimine molecules.[5b]

When the metal salicylaldimine complexes have methoxy groups in the 3,3′ positions (see, for example, Figure 1), they are potentially tetradentate donor ligands. Under such circum-

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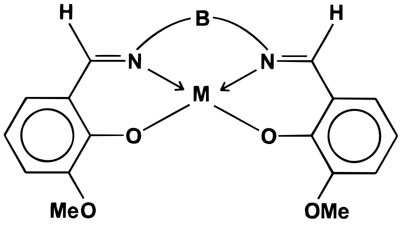

M = Co, Ni, Cu or Zn

ML_1 B = ethylene
ML_2 B = 1,2-propylene
ML_3 B = *ortho*-phenylene
ML_4 B = 1,3-propylene

Figure 1. Divalent metal salicylaldimines employed as donor ligands.

stances, the coordinated metal ion may be either retained in the plane of the donor phenolic and methoxy oxygens (as has been demonstrated in the case of diorganotin(IV)[10] and tin(II)[11] complexation) or sandwiched between two sets of Schiff base oxygens (as has been demonstrated by the complexation of lead(II) ions).[12] It would thus be anticipated that the size of an alkali metal ion would influence its mode of complexation by a metal methoxysalicylaldimine complex and that this, in turn, might have a critical influence on selectivity patterns. The present paper focuses primarily on solid-state structural aspects of adduct formation between methoxy-substituted metal salicylaldimine complexes and alkali metal ions. The study reveals novel coordination behavior of the alkali metal ions and provides some understanding of the structural factors that contribute to the formation and stoichiometry of the adducts. Furthermore, the manner in which infinite stacking assemblies are achieved in two of the adducts may serve as a useful model for the design of functional molecular assemblies.

Experimental Section

All of the salicylaldimine complexes ML_1, ML_2, ML_3, and ML_4 (see Figure 1) were prepared by standard literature methods.[13]

Preparation of Sodium Nitrate and Iodide and Tetraphenylborate Adducts. Reactions of NaA (A = nitrate or iodide) with each of the metal salicylaldimines of Figure 1 and reactions of NaBPh4 with ML_4 were carried out using a common procedure as follows. Approximately 0.8 nmol of the solid sodium salt was added to an equimolar quantity of the metal salicylaldimine complex in 30 cm^3 methanol (generally, the metal salicylaldimine was incompletely dissolved) at room temperature. In most instances, solutions were obtained and precipitation from these solutions were generally obtained only after a number of hours. After 48 h solids were isolated by filtration and dried under vacuum. Exceptions were as follows: $[Na(NO_3)\cdot NiL_3]\cdot MeOH\cdot H_2O$, $[NaI(NiL_3)_2]\cdot MeOH\cdot H_2O$, $Na(ML_4)_2]BPh_4$ (M = Ni, Cu, and Co), $[Na(ZnL_4)_2]BPh_4\cdot MeOH$, and $[NaI(NiL_2)_2]\cdot 2H_2O$ precipitated almost immediately from solution. $[Na(NO_3)\cdot NiL_2]\cdot MeOH$, $[Na(NO_3)\cdot NiL_4]\cdot MeOH$, and $[NaI(NiL_3)_2]\cdot MeOH\cdot H_2O$ were obtained as solids only after the methanol was reduced to approximately one-third of the original volume and after several days had elapsed. Adduct formation did not take place between either sodium nitrate or iodide and ZnL_4.

Preparation of Potassium and Cesium Adducts. Reactions of potassium and cesium nitrates and iodides with all of the metal salicylaldimines in Figure 1 were carried out as follows. Approximately 0.8 nmol of the solid salt was added to an equimolar quantity of the metal salicylaldimine in methanol (30 cm^3) at room temperature. In the case of the reactions involving copper, nickel, and cobalt salicylaldimines the addition of the salt resulted in instant visible color changes. After the mixture was stirred for 12 h, solid products were isolated by filtration and dried under vacuum. Unlike organotin adducts of cobalt salicylaldimines, the alkali metal adducts were not prone to cobalt oxidation. Adducts of copper and zinc were least soluble, while iodides tended to be more soluble than nitrates. Yields of adducts were always greater than 85%. In most cases reactions were also carried out with a 2-fold excess of metal salicylaldimine complex, but in no case did the excess metal salicylaldimine alter the stoichiometry of the adduct.

Reactions of M′A (M′ = K and A = thiocyanate or acetate; M′ = K or Cs and A = tetraphenylborate) with ML_4 were carried out as described for the nitrates and iodides. Thiocyanates and tetraphenylborates precipitated immediately as did $[K(acetate)\cdot ZnL_4]\cdot MeOH$. To obtain other acetates in high yield, it was necessary to reduce the volume of methanol to approximately one-quarter of the original. Potassium and cesium tetraphenylborates did not form adducts with ZnL_4.

Analytical Data for Key Complexes of the Discussion. Anal. Calcd for $Na(NO_3)/NiL_4\cdot MeOH$ ($C_{20}H_{24}N_3O_8NaNi$): C, 46.53; H, 4.45; N, 8.14. Found: C, 46.41; H, 4.31; N, 8.69. Anal. Calcd for $Na(NO_3)\cdot CuL_1\cdot MeOH$ ($C_{19}H_{22}N_3O_8CuNa$): C, 45.62; H, 4.40; N, 8.40. Found: C, 44.98; H, 4.15; N, 8.81. Anal. Calcd for $[Cs(NO_3)\cdot NiL_4]\cdot MeOH$ ($C_{58}H_{64}N_9O_{22}Cs_3Ni_3$): C, 38.42; H, 3.55; N, 6.95. Found: C, 37.99; H, 3.21; N, 6.83. Anal. Calcd for $[Na\cdot(NiL_4)_2]I\cdot EtOH\cdot H_2O$ ($C_{40}H_{48}N_4O_{10}INaNi_2$): C, 48.32; H, 4.63; N, 5.64; I, 12.77. Found: C, 48.22; H, 4.55; N, 5.77; I, 13.00. Anal. Calcd for $CsI\cdot(NiL_2)_2\cdot H_2O$ ($C_{38}H_{44}N_4O_9ICsNi_2$): C, 42.41; H, 3.90; N, 5.21; I, 11.80. Found: C, 42.64; H, 3.79; N, 4.98; I, 11.20. Anal. Calcd for $CsI_3\cdot(NiL_4)_2$ ($C_{38}H_{40}N_4O_8I_3CsNi_2$): C, 34.79; H, 3.07; N, 4.27; I, 29.02. Found: C, 35.10; H, 2.98; N, 4.42; I, 28.67. Anal. Calcd for $KiNiL_4$ ($C_{19}H_{20}N_2O_4IKNi$): C, 40.37; H, 3.54; N, 4.96; I, 22.47. Found: C, 40.24; H, 3.53; N, 4.94; I, 21.60. Anal. Calcd for $(K\cdot MeCN)_2\cdot(NiL_4)_3(BPh_4)_2$ ($C_{109}H_{106}N_7O_{12}B_2K_2Ni_3$): C, 65.59; H, 5.35; N, 5.61. Found: C, 65.21; H, 5.37; N, 6.14. Anal. Calcd for $(CsI)_2\cdot(CuL_3)_3\cdot 2H_2O$ ($C_{66}H_{58}N_6O_{14}I_2Cu_3Cs_2$): C, 42.40; H, 3.13; N, 4.50; I, 13.58. Found: C, 41.70; H, 3.06; N, 4.46; I, 15.59. Anal. Calcd for $(NaI)_2\cdot(CuL_3)_3\cdot 2H_2O$ ($C_{66}H_{58}N_6O_{14}I_2Cu_3Na_2$): C, 47.88; H, 3.50; N, 5.08; I, 15.34. Found: C, 48.13; H, 3.55; N, 5.07; I, 16.04.

Crystallization of Adducts. Attempts were made to grow crystals from the solvents methanol, ethanol, tetrahydrofuran, acetone, and acetonitrile using the following procedure. Saturated solutions of the adducts, close to the refluxing temperature of the solvent, were placed in preheated narrow-bore tubes that were immersed in hot water in a thermos flask. In this fashion suitable crystals of $Na(NO_3)\cdot NiL_4\cdot MeOH$, $Na(NO_3)$, $CuL_1\cdot MeOH$, $[Cs(NO_3)\cdot NiL_4]_3\cdot MeOH$, $CsI\cdot(NiL_2)_2\cdot H_2O$, and $KI\cdot NiL_4$ were obtained from methanol, while crystals of $[Na\cdot(NiL_4)_2]\cdot EtOH\cdot H_2O$ and $[(K\cdot MeCN)_2\cdot(NiL_4)_3](BPh_4)_2$ were obtained from ethanol and acetonitrile, respectively. It is noteworthy that $CsI\cdot(NiL_2)_2\cdot H_2O$ was obtained from the attempted crystallization of the 1/1 adduct. Poor quality crystals of $CsI\cdot NiL_4$ were obtained from methanol.

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However, when iodine was added to a hot methanolic solution of the adduct, the solubility of the adduct was greatly increased, and this led to the isolation of good quality crystals of the triiodide $CsI_3{\cdot}(NiL_4)_2$. The tetraphenylborates, on crystallization from acetonitrile, retained the 2/3 stoichiometry but contained coordinated acetonitrile, as suggested by analytical and infrared data and confirmed by the crystal structure determination of the adduct $[(K{\cdot}MeCN)_2{\cdot}(NiL_4)_3](BPh_4)_2$.

X-ray Powder Diffractometry. Powder diffraction data were collected on a JEOL model DX-Go-S diffractometer, which was modified by the incorporation of a stepping motor and a digital data collection and display system. Cu Kα ($\lambda = 1.5405$ Å) was used; a nickel filter was employed to remove Kβ. Scans using 0.1° steps and 3 s count times were employed.

Single-Crystal X-ray Diffractometry. With the exception of $CsI{\cdot}(NiL_2)_2{\cdot}H_2O$, crystals of other adducts were mounted on glass fibers. Because of instability of crystals of $CsI{\cdot}(NiL_2)_2{\cdot}H_2O$, the crystal selected for data collection was coated in liquid paraffin and mounted in a sealed capillary. Crystallographic details are in Table 1. The structures were solved by direct methods, SHELXS-86,[14] and refined by full matrix least squares using SHELXL-97.[15] SHELX operations were rendered paperless using ORTEX, which was also used to obtain the drawings.[16] Data were corrected for Lorentz and polarization effects but not for absorption. Hydrogen atoms were included in calculated positions with thermal parameters 30% larger than the atom to which they were attached. The non-hydrogen atoms were refined anisotropically. All efforts to refine the structure of $[Na(NO_3){\cdot}NiL_4]{\cdot}MeOH$ to a final value of R_1 less than approximately 10% failed, though at this point the esd values were not unreasonable. The failure to refine the structure to a more satisfactory level may be the result of the very poor diffracting power of the crystal, as a result of which there was an abnormally large number of reflections of low intensity. All calculations were performed on a Pentium PC.

Results and Discussion

The metal salicylaldimine ligands investigated in the present study are shown in Figure 1. These were chosen to investigate not only the relative effects of the metal M but also the effects of nitrogen bridging group on mode of complexation of alkali metal ions. The emphasis on the bridging group stems from the fact that studies in this laboratory have shown, as expected, that the number of carbon atoms linking the imine nitrogen atoms has a crucial bearing on the behavior of these metal salicylaldimines as ligands. For example, when the bridging group is the 1,3-propylene group, metal atoms (which are being complexed) tend to sit in the plane of the four Schiff base oxygens where they are held by strong donor bonds from the phenolic oxygen atoms and weaker donor bonds from the methoxy oxygen atoms (see, for example, refs 9 and 10). This mode of complexation was not observed thus far when the nitrogen bridging group was a two-carbon-atom bridge as, for example, in ML_1, ML_2, and ML_3. Reactions of the last metal salicylaldimines with Lewis acids generally resulted in the formation of aqua adducts with the donor water linked to the metal salicylaldimne oxygen atoms through hydrogen bonding.[17] Exceptions were found in the case of $[K{\cdot}(MnL_1)_2Fe(CN)_6]_n$ and the mixed valent lead complex $PbCl{\cdot}[NiL_1]_2(PbEt_2Cl_3)$ in which K^+ and $PbCl^+$ are sandwiched between two molecules of ML_1, being retained by eight donor bonds from Schiff base oxygen atoms.[9,11] In the former case, different substitution on the Schiff base skeleton led to adducts with different stoichiometry. Stereoelectronic modulation of the ligand is thus confirmed to be crucial for the final adducts' composition.

Table 1. Crystal Details^a

	$[Na(NO_3){\cdot}NiL_4]{\cdot}$ MeOH	$[Na(NO_3){\cdot}CuL_1]{\cdot}$ MeOH	$[Cs(NO_3){\cdot}NiL_4]_3{\cdot}$ MeOH	$[Na{\cdot}(NiL_4)_2]I{\cdot}EtOH$	$CsI{\cdot}(NiL_2)_2{\cdot}H_2O$	$CsI_3{\cdot}(NiL_4)_2$	$KI{\cdot}NiL_4$	$[K(MeCN)]_2{\cdot}$ $(NiL_4)_3](BPh_4)_2$
empirical formula	$C_{20}H_{23}N_3NaNiO_8$	$C_{19}H_{21}CuN_3NaO_8$	$C_{58}H_{56}Cs_3N_9Ni_3O_{22}$	$C_{40}H_{39}IN_4NaNi_2O_{10}$	$C_{38}H_{40}CsIN_4Ni_2O_9$	$C_{19}H_{20}Cs_{0.5}I_{1.5}N_2NiO_4$	$C_{38}H_{38}I_2K_2N_4Ni_2O_8$	$C_{43}H_{40}BKN_2NiO_4$
fw	515.11	505.92	1805.98	1003.06	1073.97	655.89	1128.14	757.39
temp, K	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
λ, Å	0.710 69	0.710 69	0.710 69	0.710 69	0.710 69	0.710 69	0.710 69	0.710 69
cryst syst	triclinic	triclinic	monoclinic	orthorhombic	orthorhombic	triclinic	triclinic	monoclinic
space group (no.)	*P*1 (2)	*P*1 (2)	$P2_1/n$ (14)	*Pbca* (61)	*Pbca* 61)	*P*1 (2)	*P*1 (2)	*C*2/*c* (15)
a, Å	7.3554(6)	7.2247(7)	12.5910(2)	14.4648(19)	15.752(3)	9.6809(11)	12.4904(17)	29.573(5)
α, deg	96.364(10)	94.804(5)	90.0000(1)	90	90	101.03	61.033(7)	90
b, Å	11.2778(10)	11.0427(6)	23.4880(2)	20.968(3)	23.276(8)	10.0015(13)	13.9363(13)	18.047(3)
β, deg	101.924(9)	98.669(7)	99.3500(1)	90	90	90.97	89.567(9)	122.860(10)
c, Å	13.562(2)	13.5610(12)	22.6660(2)	28.404(3)	25.206(6)	11.2686(13)	14.1060(12)	23.184(3)
γ, deg	96.809(10)	99.26(6)	90.0000(1)	90	90	100.55	71.579(10)	90
V, Å	1082.3(2)^3	1049.12(15)^3	6614.13(13)^3	8615.1(19)^3	9242(4)^3	1051.3(2)^3	2006.6(4)^3	10394(3)^3
Z	2	2	4	8	8	2	2	8
ρ_{calcd}, Mg/m^3	1.581	1.602	1.814	1.547	1.544	2.072	1.867	0.968
μ, mm^{-1}	0.970	1.115	2.555	1.660	2.310	4.006	2.741	0.486
R [$I > 2\sigma(I)$]	$R_1 = 0.1023$	$R_1 = 0.0389$	$R_1 = 0.0657$	$R_1 = 0.0532$	$R_1 = 0.0719$	$R_1 = 0.0667$	$R_1 = 0.0485$	$R_1 = 0.0629$
	wR2 = 0.2831	wR2 = 0.1090	wR2 = 0.1875	wR2 = 0.1402	wR2 = 0.2020	wR2 = 0.1969	wR2 = 0.1463	wR2 = 0.2013
R (all data)	$R_1 = 0.1108$	$R_1 = 0.0568$	$R_1 = 0.1118$	$R_1 = 0.1493$	$R_1 = 0.1442$	$R_1 = 0.0723$	$R_1 = 0.0578$	$R_1 = 0.1367$
	wR2 = 0.2962	wR2 = 0.1154	wR2 = 0.2100	wR2 = 0.1666	wR2 = 0.2308	wR2 = 0.2045	wR2 = 0.1535	wR2 = 0.2195

^{a} $R_1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$. $wR2 = [\Sigma_w(|F_o^2 - F_c^2)^2/\Sigma_w(|F_o^2|)^2]^{1/2}$. $w = 1/[(\sigma F_o)^2 + (aP)^2]$. The value of *aP* was obtained from structure refinement.

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Adduct formation between all of the nickel and copper salicylaldimines of Figure 1 and M′A (M′ = Na, K, and Cs; A = iodide and nitrate) was investigated. The cobalt salicylaldimine complexes were less thoroughly investigated (having discovered that these were behaving similarly to the copper and nickel salicylaldimines), and in the case of the zinc salicylaldimines, investigations were limited to the salicylaldimines ZnL_4. Since the investigation revealed that the anion was having an influence on adduct stoichiometry, the study was broadened somewhat to include adduct formation between ML_4 and both KA (A = thiocyanate or acetate) and $M'B(Ph)_4$ (M′ = Na, K, and Cs). Practically every acid/base combination studied led to the isolation of an adduct with a stoichiometry that was positively identified by a combination of powder diffractometry and elemental analytical data.

Adduct Formation by Alkali Metal Nitrates. Both potassium and cesium nitrates reacted with all of the metal Schiff base complexes to give exclusively adducts of 1/1 stoichiometry. These precipitated rapidly from methanol in greater than 90% yield. Sodium reacted with the copper, nickel, and cobalt Schiff base complexes but not with the zinc analogues; methanolic solutions containing the last complexes in combination with sodium nitrate ultimately yielded crystalline sodium nitrate. Where sodium adducts formed, they were of 1/1 stoichiometry and had much greater solubility than their potassium and cesium analogues, the one exception being $Na(NO_3)\cdot NiL_3$, which precipitated immediately from solution in greater than 90% yield. The adduct $Na(NO_3)\cdot NiL_4$ was the most soluble, remaining in methanol solution for several days following reaction.

Some significant differences were noted in the behavior of the divalent metal Schiff base complexes as donor ligands in reactions where alkali metal ions were in competition. Despite the fact that the adducts of $Cs(NO_3)$ with NiL_4, NiL_2, and CuL_3 had very low solubilities in methanol, the presence of sodium nitrate along with each of these Schiff base complexes in equimolar quantities in methanol completely prevented the precipitation of the cesium nitrate adducts. After several days, the sodium nitrate adduct crystallized from solution (as it would do in the absence of cesium nitrate), and this was followed by crystallization of cesium nitrate. When a methanol solution of sodium and cesium nitrates in equimolar quantities was added to a solution/suspension of NiL_3, the sodium adduct was preferentially precipitated (the adduct $Na(NO_3)\cdot NiL_3$, as mentioned earlier, has low solubility in methanol). However, in the case of other Schiff base complexes of this study, the presence of sodium nitrate did not prevent the precipitation of the cesium nitrate adduct nor did its presence prevent the precipitation of any potassium nitrate adducts.

In view of the fact that sodium ions are not complexed by ZnL_4 whereas potassium and cesium ions form adducts that precipitate in high yield, selective precipitation of either of these ions in the presence of sodium ions is clearly possible using the zinc salicylaldimine as the complexing ligand. However, since both potassium and cesium adducts precipitate immediately from methanolic solutions in high yield, it is clear that the metal salicylaldimines do not offer the possibility of selective precipitation of either of these ions, at least not under the conditions employed. On the other hand, from the fact that the presence of sodium ions along with NiL_4 totally suppressed the precipitation of the cesium adduct but not the potassium adduct, it would appear that this would offer a means of effecting their separation.

Rather surprisingly, however, when potassium nitrate was added to a solution containing both cesium and sodium ions along with NiL_4, the adduct that precipitated (rapidly) contained both cesium and potassium, and X-ray fluorescence spectroscopy suggested a considerable cesium content. This latter observation was further suggested by carbon, hydrogen, and nitrogen analytical data, which were approximately midway between those expected for the potassium and cesium adducts. Despite the fact that the diffraction patterns of potassium and caesium adducts of NiL_4 are strikingly similar and indeed very similar to the diffraction pattern of the mixed ion precipitate, there was sufficient evidence from weaker lines of the diffraction patterns that the mixed ion precipitate represented a new solid-state phase rather than a mixture of the two adducts. The observations suggest that the new phase may also have an infinite sandwich structure broadly similar to that of the cesium nitrate adduct (the infinite sandwich structure of this latter adduct is described later). In the case of the mixed metal adduct, both potassium and cesium ions are being sandwiched (either in random or in ordered fashion) between nickel salicylaldimine molecules.

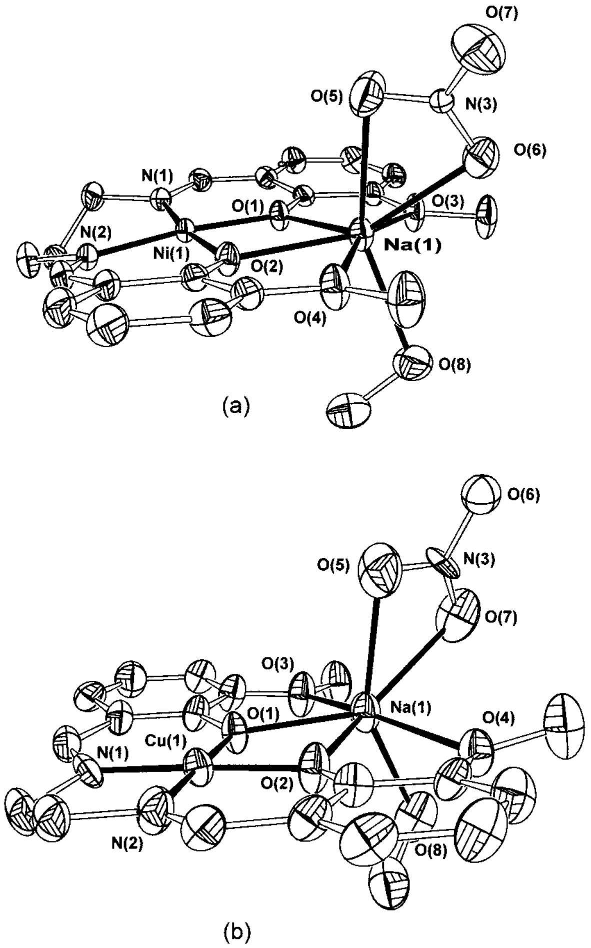

Figure 2. Asymmetric units of (a) $[Na(NO_3)(MeOH)]\cdot NiL_4$ and (b) $[Na(NO_3)(MeOH)]\cdot CuL_1$ (30% ellipsoids).

It proved to be possible to grow crystals of sodium nitrate adducts with CuL_1 and NiL_4, and their structures were determined. The asymmetric units of the adducts are in Figure 2. The geometry about sodium is extremely similar in these adducts. The sodium sits in the plane of the Schiff base oxygen atoms and is involved in electrostatic interactions with all four. Further significant interactions with two nitrate oxygen atoms and a methanol oxygen, trans to the nitrate, complete the coordination sphere, thus resulting in an unusual seven-coordination geometry about sodium. A particular point of note regarding the copper/sodium adduct is the fact that it represents

Table 2. Selected Bond Lengths (Å) for $[Na(NO_3)MeOH]\cdot NiL_4$ and $[Na(NO_3)MeOH]\cdot CuL_1$

$[Na(NO_3)MeOH]\cdot NiL_4$		$[Na(NO_3)MeOH]\cdot CuL_1$	
Ni(1)−O(1)	1.864(3)	Cu(1)−O(1)	1.8799(14)
Ni(1)−O(2)	1.864(3)	Cu(1)−O(2)	1.8855(15)
Ni(1)−N(1)	1.894(4)	Cu(1)−N(1)	1.9184(17)
Ni(1)−N(2)	1.921(3)	Cu(1)−N(2)	1.9278(17)
Ni(1)−Na(1)	3.466(2)	Cu(1)−Na(1)	3.3468(8)
Na(1)−O(1)	2.342(4)	Na(1)−O(1)	2.3197(17)
Na(1)−O(2)	2.375(3)	Na(1)−O(2)	2.3743(16)
Na(1)−O(3)	2.367(4)	Na(1)−O(3)	2.5482(16)
Na(1)−O(4)	2.397(4)	Na(1)−O(4)	2.6388(17)
Na(1)−O(5)	2.615(6)	Na(1)−O(5)	2.549(2)
Na(1)−O(6)	2.535(5)	Na(1)−O(7)	2.456(2)
Na(1)−O(8)	2.445(5)	Na(1)−O(8)	2.368(2)

the first confirmed case where a metal methoxysalicylaldimine complex containing a two-carbon-atom bridge retains the Lewis acid metal in the plane of the four ligand oxygen atoms.

The most significant difference in Na−O bond lengths between the two adducts is seen in the bonds involving the methoxy oxygens where they are much longer in the case of the copper adduct (see Table 2). The difference can be traced to the shorter imine nitrogen bridge in the copper complex, resulting in a N−Cu−N bond angle of 86.07(7)° compared to a N−Ni−N bond angle of 98.4(4)° in the nickel complex. The smaller angle results in a methoxy oxygen separation of 5.15 Å in the copper complex compared to a separation of 4.75 Å in the case of the nickel complex. The lengthening of the sodium−methoxy oxygen contacts in the sodium/copper adduct results in a strengthening of the sodium water and sodium nitrate interactions.

Of particular interest is the precise location of the sodium ion in the sodium/nickel complex compared to the location of p-block metals in their adducts with the same nickel salicylaldimine. In the case of the latter metals, and indeed silver in $Ag(NO_3)NiL_4$,[18] it is invariably found that, as a direct consequence of the trapezium arrangement of the bonding oxygen atoms, the metal is located significantly closer to the phenolic than to the methoxy oxygens to minimize repulsive interactions between bonding electrons (as predicted from Kepart's calculations[19]). That sodium does not do so is a direct consequence of the purely electrostatic nature of the Na−O interactions.

It has recently been shown that $Ni(MeOsalNH)_2$ [HMeOsalNH = 3-methoxy salicyideneamine) forms an adduct with sodium perchlorate.[20] The location of the sodium ion in this complex is very similar to that in the present nickel−sodium adduct. However, the perchlorate provides only one significant Ni−O interaction, and this, coupled with an interaction with a water molecule, resulted in a coordination number of 6 for sodium (in an unusual pentagonal pyramidal geometry) compared with 7 in the present structures.

Although it proved to be possible to grow crystals of several other alkali metal nitrate adducts, it was only in the case of the cesium nitrate adduct of NiL_4 that crystals suitable for a crystallographic study were obtained. The asymmetric unit of this fascinating adduct (see Figure 3 and Table 3 for selected bond lengths) corresponding to the formula $\{[Cs(NO_3)\cdot NiL_4\}_3\cdot MeOH$ is part of an infinite sandwich structure generated by the 2_1 axis lying close to the cesium ions; the cesium ions are in an oval-shaped helical array about the 2_1 axis. This is the first example of a metal salicylaldimine ligand being involved in an infinite sandwich structure, though not the first such structure involving cesium ions. The first infinite sandwich structure containing cesium ions was recently reported employing a crown ether as ligand.[21] The three crystallographically independent cesium ions are in similar locations insofar as they are each sandwiched between two sets of five oxygen atoms. Four of the five oxygens in each set belong to a nickel salicylaldimine molecule while the fifth belongs to a nitrate group, the three nitrate oxygens in question being O(14), O(18),

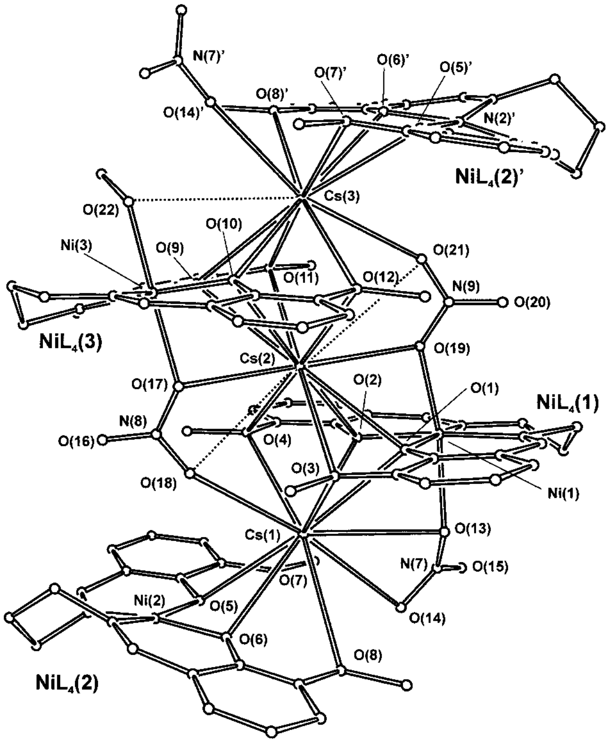

Figure 3. Section of the infinite sandwich structure of $[Cs(NO_3)\cdot NiL_4]_3\cdot MeOH$ (atoms portrayed as spheres for clarity). Dotted lines correspond to contacts greater than 3.5 Å.

Table 3. Selected Bond Lengths (Å) for $[Cs(NO_3)\cdot NiL_4]_3\cdot MeOH$

Cs(1)−O(1)	3.142(6)	Cs(1)−O(2)	3.007(6)
Cs(1)−O(3)	3.218(7)	Cs(1)−O(4)	3.188(6)
Cs(1)−O(5)	3.253(6)	Cs(1)−O(6)	3.047(6)
Cs(1)−O(7)	3.391(7)	Cs(1)−O(8)	3.361(8)
Cs(1)−O(13)	3.297(8)	Cs(1)−O(14)	3.268(8)
Cs(1)−O(18)	3.138(8)	Cs(2)−O(1)	2.989(6)
Cs(2)−O(2)	3.136(6)	Cs(2)−O(3)	3.286(7)
Cs(2)−O(4)	3.208(7)	Cs(2)−O(9)	3.037(6)
Cs(2)−O(10)	3.232(6)	Cs(2)−O(11)	3.313(7)
Cs(2)−O(12)	3.232(7)	Cs(2)−O(17)	3.110(8)
Cs(2)−O(18)	3.589(10)	Cs(2)−O(19)	3.193(8)
Cs(2)−O(21)	3.934(8)	Cs(3)−O(5)′	3.105(6)
Cs(3)−O(6)′	3.215(6)	Cs(3)−O(7)′	3.237(6)
Cs(3)−O(8)′	3.131(7)	Cs(3)−O(9)	3.204(7)
Cs(3)−O(10)	3.033(6)	Cs(3)−O(11)	3.164(7)
Cs(3)−O(12)	3.161(7)	Cs(3)−O(14)′	3.191(8)
Cs(3)−O(21)	3.269(9)	Cs(3)−O(22)	4.006(8)
Ni(1)−O(1)	1.996(5)	Ni(1)−O(2)	1.991(5)
Ni(1)−N(1)	2.015(7)	Ni(1)−N(2)	2.042(8)
Ni(1)−O(13)	2.268(8)	Ni(1)−O(19)	2.133(8)
Ni(2)−O(5)	1.866(5)	Ni(2)−O(6)	1.852(6)
Ni(2)−N(3)	1.881(8)	Ni(2)−N(4)	1.868(7)
Ni(3)−O(9)	1.991(6)	Ni(3)−O(10)	2.007(6)
Ni(3)−N(5)	2.038(8)	Ni(3)−N(6)	2.042(8)
Ni(3)−O(17)	2.209(8)	Ni(3)−O(22)	2.153(7)

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and O(21). The oxygens of each set are approximately coplanar and lie at the corners of an elongated pentagon, the elongation in each case originating from the displacement of the nitrate oxygen from the more ideal pentagonal geometry location. As a result of the sandwich arrangement so described, each cesium has a coordination geometry that is most aptly described as pentagonal antiprismatic. Cs−O interactions within these coordination environments are generally strong, apart from those involving O(18) and O(21). There are, however, additional Cs−O contacts resulting from nitrate and methanol (see Table 3) such that the overall coordination geometries of Cs(1) and Cs(3) can be described as monocapped pentagonal antiprismatic, while that of Cs(2) can be described as bicapped pentagonal antiprismatic.

The salicylaldimine oxygen atoms provide, on average, much stronger contacts with the cesium ions than do the crown ether oxygens in the infinite sandwich structure of $[\mathrm{Cs(18\text{-}crown\text{-}6)}]^+[\mathrm{tcNCl_4}]^-$[21]. In the case of the structure of the latter, three of the oxygens provide Cs−O contacts of 3.34(1), 3.34(1), and 3.35(1) Å (most of the Cs−O distances involving salicylaldimine oxygens are less than these values), while the other three provide significantly longer contacts of 3.66(1), 3.67(1), and 3.68(1) Å. All of the $\mathrm{Cs^+-Cs^+}$ separations in the present structure (3.872, 3.909, and 4.050 Å) are smaller than the $\mathrm{Cs^+-Cs^+}$ separation of 4.275 Å in the crown ether structure.

Apart from forming close contacts with cesium ions, O(13) and O(19) and O(17) also form bonds to nickel ions. The former two oxygens complete the octahedral geometry about Ni(1), while the latter oxygen, along with the methanol oxygen O(22), complete the octahedral geometry about Ni(3). There are no bonds to Ni(2) other than those provided by the Schiff base ligand. Thus, the infinite sandwich structure consists of pairs of nickel salicylaldimines [nickel salicylaldimines (1) and (3) with octahedral nickel separated by single square-planar nickel salicylladimines [nickel salicylaldimine (2)].

In view of the 1/1 stoichiometry of all of the adducts of both cesium and potassium nitrate with the metal salicylaldimines of Figure 1 and the apparent inability of these large ions to be located within the plane of the Schiff base oxygen atoms, the coordination requirements of the ions are most easily achieved in infinite sandwich structures broadly similar to that already described for the cesium nitrate adduct of $\mathrm{NiL_4}$ or that of $\mathrm{KI{\cdot}NiL_4}$ (to be described later). The marked similarity of the powder diffraction patterns of all of the 1/1 adducts, including that of $\mathrm{[Cs(NO_3){\cdot}NiL_4]{\cdot}MeOH}$, is consistent with, though not total proof of, a common infinite sandwich type structure. It is clear, however, from magnetic data that while the adducts may share a common infinite sandwich type structure they do not feature the diversity of nitrate roles that led to three nickel environments in the cesium nitrate adduct of $\mathrm{NiL_4}$.

The adduct $\mathrm{K(NO_3){\cdot}NiL_4}$ has a magnetic moment of 3.31 B M per nickel, while the adducts $\mathrm{Cs(NO_3){\cdot}CoL_4}$ and $\mathrm{Cs(NO_3){\cdot}CoL_4}$ have magnetic moments of 4.97 and 4.84 B M per cobalt, respectively, indicating that these do not have the complication of square-planar geometries (about the transition metal ions) coexisting with other geometries within their structures. However, in view of the magnetic moments and the apparent anhydrous nature of the adducts, it is clear that the nitrates do coordinate to the nickel and cobalt centers.

By contrast, nitrate coordination to the transition metal ions does not occur in adducts containing $\mathrm{ML_1}$, $\mathrm{ML_2}$, and $\mathrm{ML_3}$ (M = Ni or Co), since the nickel adducts are diamagnetic and the cobalt analogues are low-spin complexes. These observations are in accord with our earlier observations that indicate that a metal atom in a salicylaldimine complex having a two-carbon-atom (imine) nitrogen-bridging group is very much less likely than the metal of an analogous complex with a three-carbon-atom bridge to expand its coordination beyond 4 when the salicylaldimine complex adopts a donor ligand role.

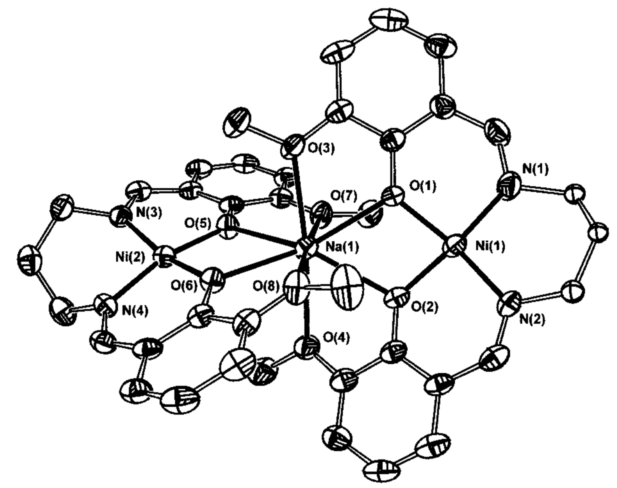

Figure 4. Asymmetric unit of $\mathrm{[Na{\cdot}(NiL_4)_2]I{\cdot}EtOH}$ (30% ellipsoids). The iodide and lattice ethanol are omitted.

Table 4. Selected Bond Lengths (Å) for $\mathrm{[Na{\cdot}(NiL_4)_2]I{\cdot}EtOH}$

Ni(1)−O(1)	1.847(4)	Ni(2)−O(5)	1.846(4)
Ni(1)−O(2)	1.864(4)	Ni(2)−O(6)	1.839(4)
Ni(1)−N(1)	1.868(6)	Ni(2)−N(3)	1.863(5)
Ni(1)−N(2)	1.886(5)	Ni(2)−N(4)	1.866(4)
Ni(1)−Na(1)	3.530(2)	Na(1)−Ni(2)	3.472(2)
Na(1)−O(1)	2.424(4)	Na(1)−O(5)	2.412(4)
Na(1)−O(2)	2.452(4)	Na(1)−O(6)	2.413(4)
Na(1)−O(3)	2.486(5)	Na(1)−O(7)	2.519(5)
Na(1)−O(4)	2.493(5)	Na(1)−O(8)	2.544(4)

Adduct Formation by Alkali Metal Iodides. Both potassium and cesium iodides, like their nitrate analogues, reacted with the metal salicylaldimines to yield adducts that precipitated rapidly from methanol but in somewhat reduced yields (ranging from approximately 80% to 85%). Most of the adducts were of 1/1 stoichiometry, but there were notable exceptions. Both potassium and cesium iodides formed 1/2 adducts with $\mathrm{NiL_3}$, and potassium iodide formed an adduct with the same stoichiometry with $\mathrm{CuL_3}$. Cesium iodide formed an adduct of 2/3 stoichiometry with $\mathrm{CuL_3}$.

Adducts of sodium iodide precipitated from solution very slowly except for those involving $\mathrm{NiL_2}$ and $\mathrm{NiL_3}$, which precipitated very rapidly. All of the sodium adducts with the nickel salicylaldimines were of 1/2 stoichiometry, whereas those with the copper salicylaldimines were of 1/1 stoichiometry except for the adduct with $\mathrm{CuL_3}$, which appears to be of 2/3 stoichiometry. As had been the case with sodium nitrate, sodium iodide did not form adducts with $\mathrm{ZnL_4}$.

In several instances, crystals of reasonable quality were obtained, thus allowing the structures of the sodium and potassium iodide adducts of $\mathrm{NiL_4}$, the cesium iodide adduct with $\mathrm{NiL_2}$, and the cesium triiodide adduct of $\mathrm{NiL_4}$ to be determined crystallographically.

The asymmetric unit of the 1/2 adduct of sodium iodide with $\mathrm{NiL_4}$ is shown in Figure 4, and selected bond lengths are in Table 4. Iodide has no meaningful contacts with either sodium or nickel but is involved in weak hydrogen-bonding interactions with water and ethanol molecules of crystallization (these are omitted from Figure 4). Two nickel salicylaldimines approach

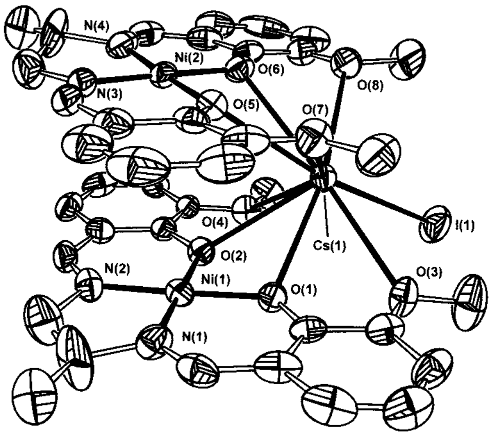

Figure 5. Asymmetric unit of CsI·$(NiL_2)_2$·H_2O (30% ellipsoids) with the water molecule omitted.

Table 5. Selected Bond Lengths (Å) for CsI·$(NiL_2)_2$·H_2O

Cs(1)−O(1)	3.072(7)	Ni(1)−O(1)	1.851(7)
Cs(1)−O(2)	3.063(7)	Ni(1)−O(2)	1.867(7)
Cs(1)−O(3)	3.139(9)	Ni(1)−N(1)	1.821(10)
Cs(1)−O(4)	3.142(8)	Ni(1)−N(2)	1.846(9)
Cs(1)−O(5)	3.111(7)	Ni(2)−O(5)	1.869(7)
Cs(1)−O(6)	3.081(7)	Ni(2)−O(6)	1.843(8)
Cs(1)−O(7)	3.175(9)	Ni(2)−N(3)	1.841(12)
Cs(1)−O(8)	3.120(9)	Ni(2)−N(4)	1.845(13)
Cs(1)−I(1)	4.090(1)		

the sodium ion such that the planes defined by their oxygen atoms are inclined at an angle of approximately 81.5° to each other. Sodium is within each of these planes and is located such that there is reasonable uniformity in the sodium−oxygen electrostatic interactions (Na−O contacts range from 2.405(7) to 2.537(8) Å). To achieve this, sodium is located close to the outer edge of each of the trapeziums of oxygen atoms such that the methoxy oxygens of each ligand subtend angles of 173.3(1)° and 175.9(3)° at sodium. As a result of the interlacing of the two trapeziums, sodium achieves fairly regular dodecahedral geometry, an unusual coordination geometry for sodium. It seems highly likely that all of the sodium iodide adducts of 1/2 stoichiometry have the same dodecahedral coordination geometry about sodium. A more usual six-coordinate geometry could easily have been achieved by sodium by forming 1/1 addition complexes with the Schiff base oxygens and two water oxygen atoms involved in bonding interactions with the cation. This probably is the situation in the 1/1 adducts $(Na·CuL_2)I·2H_2O$ and $(Na·CuL_4)I·2H_2O$.

Although the adduct that immediately precipitated from solution following reaction of cesium iodide with NiL_2 was of 1/1 stoichiometry, the adduct that was obtained from slow crystallization was the 1/2 adduct CsI·$(NiL_2)_2$·H_2O. The structure of this adduct is strikingly different from that of the sodium iodide adduct structure described above, the difference being dictated by the much larger size of cesium relative to that of sodium. In this case (see Figure 5) the cesium ion is sandwiched between two sets of Schiff base oxygen atoms with Cs−O contacts ranging from 3.06(1) to 3.21(1) Å (see Table 5); these are comparable with the shorter Cs−O contacts in the cesium nitrate structure described earlier. Each set of Schiff base oxygens is essentially coplanar, and these planes are essentially parallel. The iodide is 0.24 Å from the plane defined by the set of oxygens O(1)−O(4) and situated at distances of 4.51 and 4.52 Å from the methoxy oxygens O(3) and O(4), respectively. There is a Cs−I contact at 4.090(2) Å, which brings the overall cesium coordination number to 9. Cesium is 1.67 and 1.78 Å from the planes defined by O(1)−O(4) and O(5)−O(8), respectively, the shorter distance probably resulting from the extra attraction to the iodide lying close to the plane defined by O(1)−O(4).

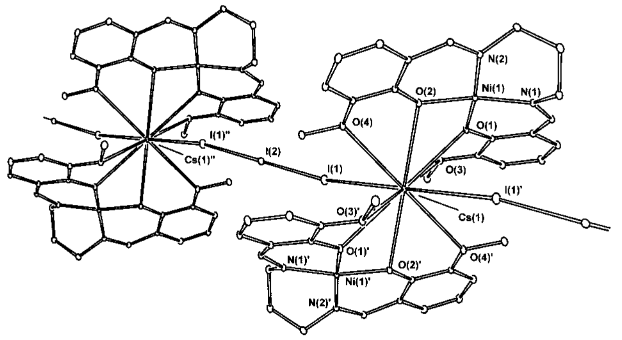

Figure 6. Section of the nominal chain polymeric structure of CsI_3·$((NiL_4)_2$· (atoms portrayed as spheres for clarity).

Table 6. Selected Bond Lengths (Å) for CsI_3·$(NiL_4)_2$

Cs(1)−O(1)	3.027(3)	Cs(1)−O(2)	3.149(4)
Cs(1)−O(3)	3.262(4)	Cs(1)−O(4)	3.127(4)
Cs(1)−I(1)	3.9666(6)	I(1)−I(2)	2.9047(5)
Ni(1)−O(1)	1.861(3)	Ni(1)−O(2)	1.862(3)
Ni(1)−N(1)	1.883(4)	Ni(1)−N(2)	1.881(4)

The 1/1 addition complex formed between cesium iodide and NiL_4 had limited solubility in methanol, and all attempts to grow single crystals from this solvent resulted in the formation of small clumps of twinned crystals. Addition of I_2 to the solution greatly enhanced the solubility of the cesium iodide adduct, and from the more concentrated solution, crystals of the adduct CsI_3·$(NiL_4)_2$ were obtained. This is an interesting adduct having a nominal chain polymeric structure as a result of bridging triiodide groups. A section of the polymeric chain is shown in Figure 6, while selected bond lengths are in Table 6. The chain packing arrangement coupled with short aromatic ring contacts suggests the presence of attractive π-aromatic interactions linking all neighboring chains. Both cesium and the central iodine of the triiodide groups are on centers of inversion. Thus, the structure contains true triiodide ions with I−I bond lengths of 2.904(1) Å.

As had been the case in the cesium iodide adduct structure described above, the cesium ions are sandwiched between two sets of Schiff base oxygens giving eight Cs−O contacts with contact distances in the range 3.027(3)−3.262(4) Å. Each set of Schiff base oxygens is essentially coplanar, and these planes are close to being parallel. An iodine of a triiodide ion lies close to each of these planes, and these iodine atoms give rise to Cs−I contacts at 3.967(1) Å, compared with a Cs−I contact at 4.090(2) Å in the iodide structure discussed above. Cesium is 1.81 Å from the planes defined by the Schiff base oxygens. It is 10-coordinate, and the coordination geometry can be described as distorted pentagonal antiprismatic, a geometry that is very similar to that in the 1/2 adduct of potassium chloride with *O*,*O*′-catecholdiacetic acid.[22] However, the resemblance between these two structures runs deeper than this. Potassium is sandwiched between two sets of oxygens disposed toward the corners of a trapezium, quite similar to that defined by the Schiff base oxygens, and just as the iodine atoms complete the pentagonal faces of the coordination polyhedron in the present structure, oxygen atoms from neighboring molecules complete the pentagonal faces in the structure of the potassium adduct.

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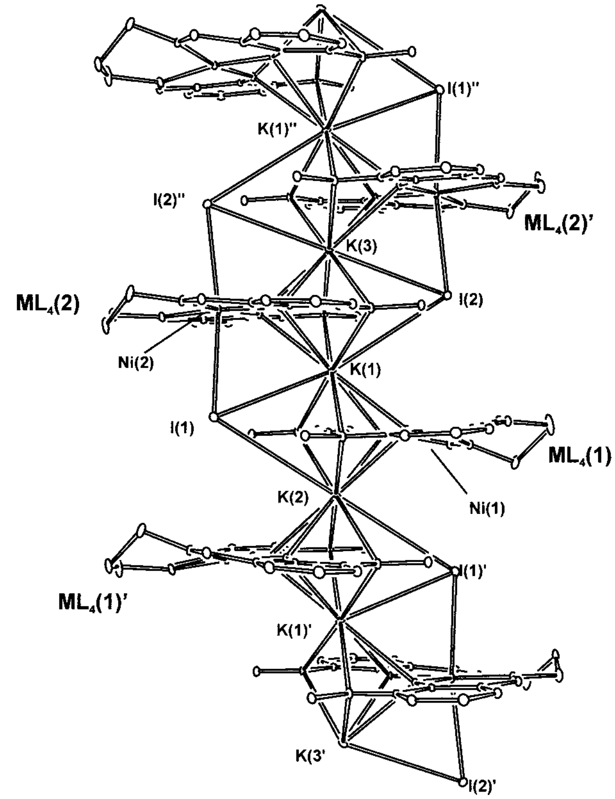

Figure 7. Section of the infinite sandwich structure of KI·NiL$_4$ (10% ellipsoid outlines).

The most intriguing and crystallographically the most complicated structure of this study is that of the 1/1 adduct of potassium iodide with NiL$_4$. In broad terms, it is similar to the structure of the cesium nitrate adduct with NiL$_4$ insofar as it is an infinite sandwich structure (see Figure 7) in which potassium ions are sandwiched between sets of salicylaldimine oxygen atoms. All of the oxygen are involved in significant electrostatic interactions with the cations. Furthermore, as had been the case with the cesium nitrate structure, ion pairing is evident.

The asymmetric unit consists of two nickel salicylaldimine complexes, ML$_4$(1) and ML$_4$(2) in Figure 7, two iodide ions, I(1) and I(2), and three potassium ions. Two of the latter, K(2) and K(3), are on centers of inversion and the third, K(1), is close to a center of inversion. Potassium ions alternate through the sandwich structure in the order K(1), K(2), K(1), K(3) etc. Considerable complication is introduced by the fact that both iodides are disordered over two positions with site occupancies of 70% and 30%. In Figure 7 the iodides are shown in their 70% positions.

With the iodides located in their 70% occupancy sites, all three potassium ions achieve 10 coordination as a result of eight contacts with the Schiff base oxygens, those to the phenolic oxygens being on average approximately 0.2 Å shorter than those to the methoxy oxygens, and two contacts with iodide ions. In the case of K(2) both K−I distances are long at 4.196 Å, while for K(1) one of the K−I distances is long at 4.178 Å. With the iodide ions in their 30% occupation positions, the coordination numbers of all potassium ions remains unaltered, but it is now K(3) rather than K(2), which has the two long K−I contacts (see Table 7 for selected bond lengths).

With the iodides located in their 70% occupancy sites, Ni(2) achieves six coordination as a result of the Ni−O and Ni−N bonds within the metal salicylaldimine molecule and trans Ni(2)−I(1) and Ni(2)−I(2) bonds with bond lengths of 3.0655(8) and 3.0135(7) Å, respectively. By contrast, there are no significant interactions between Ni(1) and iodide ions, and thus, this nickel remains square-planar. As a result of the centers of inversion on K(2) and K(3), pairs of nickel salicylaldimine molecules exist with octahedral nickel and these alternate with pairs containing square-planar nickel. When both iodide ions occupy their 30% occupation sites, Ni(2) becomes diamagnetic and Ni(1) becomes octahedrally coordinated as a result of the formation of Ni(1)−I(1) and Ni(1)−I(2) bond lengths of 3.1760(9) and 3.0367(18) Å, respectively [note that these bond lengths are slightly different from those that had been to Ni(2)]. Thus, the infinite sandwich still consists of pairs of square-planar nickel salicylaldimines alternating with pairs of octahedral nickel salicylaldimines. Since the iodides are crystallographically independent, the possibility must also be considered where one iodide is in its 70% occupation site while the other is in its 30% occupation site. Under such circumstances, irrespective of which iodide is in the 70% occupation site, all nickels have square pyramidal geometry.

Table 7. Selected Bond Lengths (Å) for KI·NiL$_4$[a]

K(1)−O(1)	2.886(2)	K(1)−O(2)	2.856(2)
K(1)−O(3)	3.056(2)	K(1)−O(4)	3.244(3)
K(1)−O(5)	2.819(2)	K(1)−O(6)	2.821(2)
K(1)−O(7)	3.171(3)	K(1)−O(8)	3.060(2)
K(1)−I(1)	3.7111(10)	K(1)−I(2)	4.180(1)
K(2)−O(1)	2.812(2)	K(2)−O(2)	2.826(2)
K(2)−O(3)	3.263(3)	K(2)−O(4)	2.989(2)
K(2)−I(1)	4.196(1)	K(3)−O(5)	2.806(2)
K(3)−O(6)	2.818(2)	K(3)−O(7)	3.067(2)
K(3)−O(8)	3.218(2)	K(3)−I(2)	3.7892(6)
Ni(1)−O(1)	1.898(2)	Ni(1)−O(2)	1.897(2)
Ni(1)−N(1)	1.911(3)	Ni(1)−N(2)	1.920(3)
Ni(1)−I(1a)′	3.1760(9)	Ni(1)−I(2a)	3.0367(18)
Ni(2)−O(5)	1.975(2)	Ni(2)−O(6)	1.970(2)
Ni(2)−N(3)	2.016(3)	Ni(2)−N(4)	1.994(3)
Ni(2)−I(1)	3.0655(8)	Ni(2)−I(2)′	3.0135(7)

[a] O(1) and O(2) are the phenolic oxygens and O(3) and O(4) the methoxy oxygens of NiL$_4$(1). O(5) and O(6) are the phenolic oxygens and O(7) and O(8) the methoxy oxygens of NiL$_4$(2) (see Figure 7).

None of the 1/1 adducts of CsI and KI contain solvent or water molecules that could contribute to the coordination spheres of the large potassium and cesium ions. Thus, the coordination demands of the cations are most easily achievable in an infinite sandwich structure, broadly similar to the two infinite sandwich structures that were confirmed by the crystallographic data. The pronounced similarity of the powder diffraction patterns of potassium and caesium nitrate adducts extends to those of the iodide analogues, and this is consistent with (though not necessarily proof of) a common structural type. Magnetic data do however point to differences in the role of iodide in the adduct structures.

In contrast to the paramagnetic nature of KI·NiL$_4$, the cesium iodide analogue is diamagnetic, as are all other 1/1 adducts of cesium iodide and potassium iodide with NiL$_1$, NiL$_2$, and NiL$_3$. Thus, only in the case of the potassium iodide structure do the iodide ions coordinate to nickel. If the iodide ions in the diamagnetic adducts are located close to the planes of the Schiff base oxygen atoms, as they do in the 1/2 adduct of cesium iodide with NiL$_2$ (the structure of which was described earlier), they can be involved in electrostatic interactions with the alkali metal ions without forming bonds to nickel. Presumably this is the situation that prevails in the diamagnetic adducts.

The 1/1 adducts of cesium and potassium iodides with CoL$_4$ contain high-spin cobalt with magnetic moments of 4.97 and 4.80 B M per cobalt, respectively, whereas all of the other 1/1 adducts with CoL$_1$, CoL$_2$, and CoL$_3$ contain low-spin cobalt.

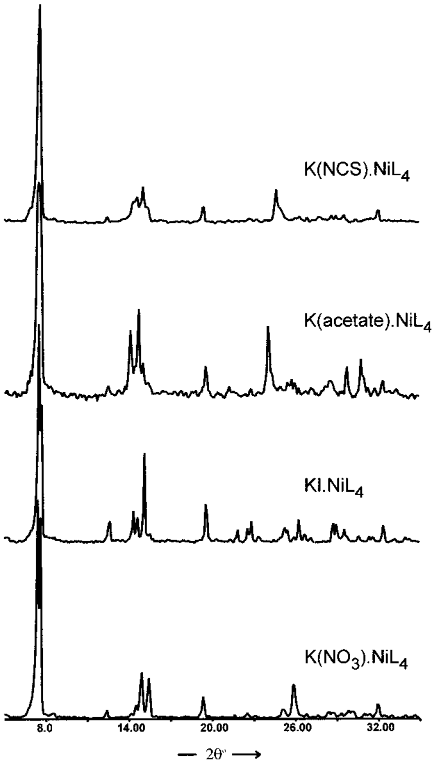

Figure 8. Powder diffraction patterns of potassium salt adducts of NiL_4.

The latter complexes, in all probability, have iodide ions in locations similar to those in the nickel analogues. In view of the absence of water and methanol in the lattices of the high-spin complexes, it is clear that the iodide ions are located such that they form Co−I bonds. In view of the normal magnetic moments of these adducts, the iodide ions clearly do not exhibit the disorder featured in the structure of $KI{\cdot}NiL_4$, thus contributing to its abnormally low magnetic moment of 2.57 B M per nickel ion.

Reactions of Potassium Thiocyanate and Acetate with ML_4. Potassium thiocyanate and acetate reacted with ML_4 to give exclusively 1/1 adducts. The potassium acetate adducts with ML_4, where M = Cu, Co, and Ni, were extremely soluble, whereas all other adducts precipitated rapidly from solution. The potassium thiocyanate and acetate adducts of NiL_4 each had magnetic moments of 3.2 B M, whereas the cobalt analogues were high-spin with magnetic moments of 4.6 and 4.7 B M, respectively. Since these adducts apparently contain neither donor solvent molecules nor water, the implication is that the anions are coordinated to the transition metal. Presumably they are also involved in electrostatic interactions with the potassium ions.

The powder diffraction patterns of the potassium thicyanate and acetate adducts bear a remarkable resemblance, and indeed, this resemblance extends to diffraction patterns of all of the nitrate and iodide adducts. The diffraction patterns of the potassium adducts of NiL_4 shown in Figure 8 clearly illustrate this point where it is seen that the resemblance is particularly pronounced in the 2θ range 5−25°. A possible reason for the resemblance of the diffraction patterns can be appreciated by reference to Figure 9, which shows sections of the infinite sandwich arrays for the cesium nitrate and potassium iodide adducts of NiL_4 when viewed along the direction of propagation of the sandwiches. The most striking observation is the similarity of the cross-sectional shapes of the columns that the infinite sandwiches generate. This shape is dictated by the alkali metal ions, demanding that successive nickel salicylaldimine molecules be approximately related by 180° rotations. Since the columns in each of the structures have essentially the same shape, they pack very similarly in each of the lattices. Figure 10 shows how neighboring columns, which provide the total content of a row of unit cells stacked parallel to the *b* axis, are mutually arranged in the cesium nitrate adduct structure. In the extended structure this gives a packing arrangement resembling the intermeshing of cogwheels. Since the nitrate and iodide ions are within the columnar structures, they clearly have little influence on the lattice packing. If the thiocyanates and acetates adducts adopt the infinite sandwich structures, these anions can likewise remain within the columnar structures.

Reactions of Alkali Metal Tetraphenylborates with ML_4. A necessary condition for efficient lattice packing of infinite sandwich columns, such as shown in Figure 10, is that the anions are relatively small and contained within the boundaries of the columnar sandwich assemblies. This is achieved by ion-pairing and, in some cases, by the additional complexation of the anion to the transition metal. The question arises as to what type of stoichiometry and structures would be preferred if the anions were too bulky to be accommodated comfortably within the boundaries of the columns, and with this in mind attention was focused on tetraphenylborate salts.

$NaBPh_4$ reacted with all of the complexes ML_4 to give 1/2 adducts, whereas cesium and potassium tetraphenylborates reacted when M was Cu, Co, or Ni to give adducts of 2/3 stoichiometry. Reactions with ZnL_4 yielded surprising results. Sodium tetraphenylborate yielded an adduct with the zinc salicylaldimine, whereas the nitrate and iodide salts failed to do so. The reverse situation was observed in the case of the potassium and cesium adducts. Potassium and cesium tetraphenylborates failed to give adducts with this zinc salicylaldimine, whereas the nitrate and iodide salts readily yielded 1/1 adducts. The fact that ZnL_4 was the only complex that in any case failed to yield adducts suggests that of all the salicylaldimine complexes investigated, it is the weakest donor ligand toward alkali metals.

Adduct formation in the present study implies that the adduct precipitated in preference to starting materials, and thus, all of the factors that contribute to the lattice energies of starting materials and adducts have an important bearing on the outcome. While the strength of electrostatic interaction between the metal salicylaldimine complex and cation is one of these factors, other factors such as ion-pairing, donor bond formation between the anion and the transition metal, and lattice packing are also important factors. The latter three factors assume increasing significance as the interaction between the salicylaldimine and cation weakens. Thus, the inability of either sodium iodide or nitrate to yield an adduct with ZnL_4 when sodium tetraphenylborate did so may well reflect a higher lattice energy associated with the packing of $Na(ZnL_4)_2$ and tetraphenylborate groups than the packing of the same complex cation with either iodide or nitrate. The ability to isolate adducts of cesium and potassium iodides and nitrates with ZnL_4, contrasting with the inability to do so with either sodium nitrate or sodium iodide, may reflect a very favorable packing energy associated with the packing of the infinite sandwich assemblies as described earlier. Furthermore, the inability of potassium and cesium tetraphenylborates to yield adducts with ZnL_4 may then be attributed to the fact that this favorable packing is now no longer possible following the introduction of the bulky tetraphenylborate groups.

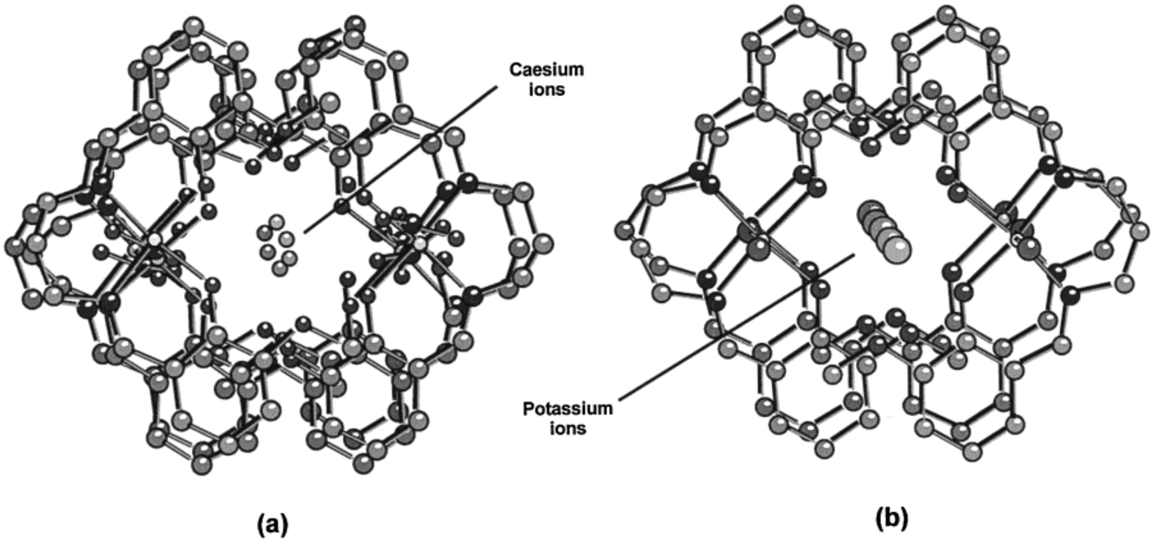

Figure 9. Comparison of molecular stacking in the cesium nitrate and potassium iodide adducts [parts a and b, respectively] of NiL_4 when viewed along stacking directions.

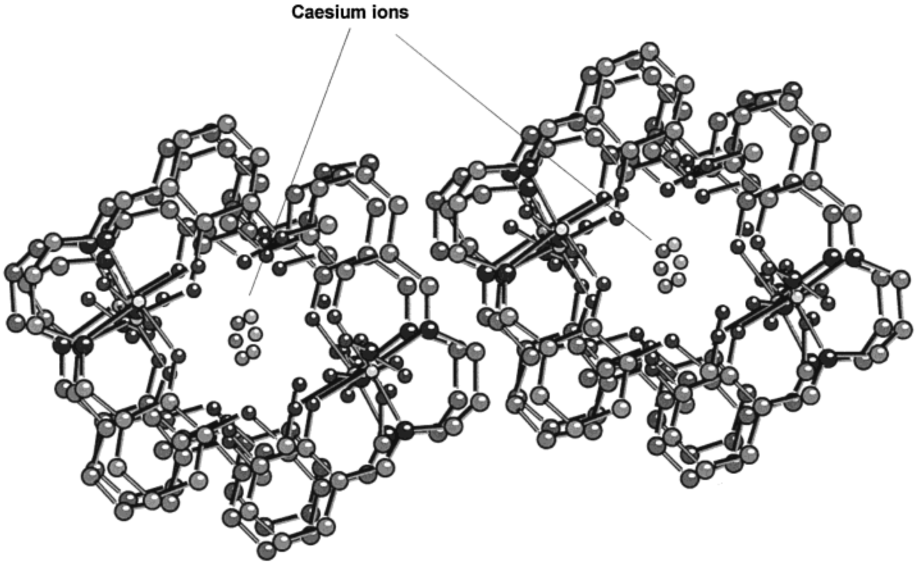

Figure 10. Adjacent columns, providing the contents of a row of unit cells stacked along the *b* axis in the structure of $[Cs(NO_3)\cdot NiL_4]_3\cdot MeOH$.

It seems highly likely that all of the sodium tetraphenylborate adducts have sodium in the same type of dodecahedral environment as that described for $Na(NiL_4)_2I\cdot EtOH\cdot H_2O$ (in no case did it prove possible to obtain suitable crystals of a sodium tetraphenylborate adduct for a crystallographic study). The nickel adduct is diamagnetic while cobalt in the cobalt adducts is low-spin, thus indicating that the metals are in square-planar environments in these adducts, as was nickel in the sodium iodide adduct.

It did not prove to be possible to obtain crystals of any of the potassium or cesium tetraphenylborates adducts from methanol, but when acetonitrile was employed as a preparative solvent, adducts precipitation was rapid and, following removal of these solids, crystals were observed, in some instances, to grow slowly from the filtrates. In this fashion reasonable quality crystals of the potassium tetraphenylborate adduct with NiL_4 were obtained, one of which was selected for a crystallographic study.

The asymmetric unit of this adduct consists of a full nickel salicylaldimine molecule, a potassium ion with an acetonitrile molecule coordinated to it, and half of a second nickel salicylaldimine molecule, the other half being generated by a crystallographic 2-fold axis passing through nickel. In actual fact, this 2-fold axis generates the full cation (see Figure 11) consisting of three nickel salicylaldimine molecules and two potassium ions (with associated acetonitrile molecules) in a club sandwich type structure, thus accounting for the 2/3 stoichiometry.

Each of the symmetry-related potassium ions is involved in electrostatic interactions with all four Schiff base oxygens of a terminal nickel salicylaldimine molecule, these interactions, on average, being somewhat stronger with the phenolic oxygens (see Table 8), while it is also involved in interactions with three oxygens of the central nickel salicylaldimine. On average, the K−O distances to these central oxygens are greater than those to the terminal oxygens, an observation that can be rationalized on the basis of the central oxygens being involved in interactions with two potassium ions. Furthermore, there may be a degree of repulsion between the two potassium ions. The coordination of each potassium is increased to 8 as a result of an interaction with an acetonitrile molecule.

The three metal salicylaldimine molecules are arranged such that on each wing of the cation there are three phenyl groups

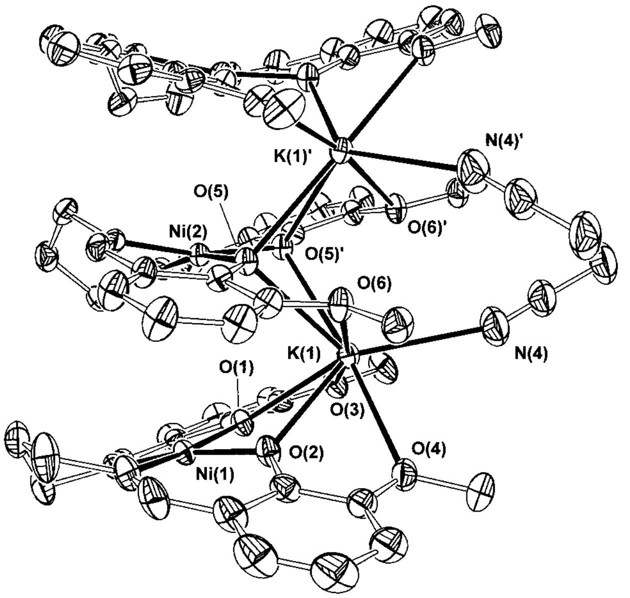

Figure 11. Triple decker structure of $[K(MeCN)]_2 \cdot (NiL_4)_3$ (40% ellipsoids).

Table 8. Selected Bond Lengths (Å) for $[K(MeCN)]_2 \cdot (NiL_4)_3(BPh_4)_2$

K(1)−O(1)	2.736(3)	K(1)−O(2)	2.663(3)
K(1)−O(3)	2.746(3)	K(1)−O(4)	2.901(4)
K(1)−O(5)	2.859(3)	K(1)−O(6)	2.894(3)
K(1)−O(5)′	2.901(3)	K(1)−O(6)′	3.750(4)
K(1)−N(4)	2.981(7)	Ni(1)−O(1)	1.862(3)
Ni(1)−O(2)	1.849(3)	Ni(1)−N(1)	1.860(4)
Ni(1)−N(2)	1.904(4)	Ni(2)−O(5)	1.851(3)
Ni(2)−N(3)	1.872(4)		

arranged with their planes being close to parallel while there are a number of C−C and C−N contacts between neighboring aromatic and azomethine carbon and nitrogen atoms lying in the range 3.417−3.0.9 Å. These features suggests the possibility of net attractive π interactions.[24]

All of the potassium and cesium tetraphenylborate adducts isolated from acetonitrile, being of the same stoichiometry and containing acetonitrile (as suggested by both infrared spectroscopy and analytical data) presumably share the same type of club sandwich type structure as that described above. The adducts isolated from methanol show no evidence, from analytical or infrared data, for either methanol or water molecules that could adopt the role of acetonitrile in the structure described. The loss of the coordinating donor molecule probably results in changes in salicylaldimine conformation and relative orientations such that the alkali metals are coordinated by eight salicylaldimine oxygens as they are in the infinite sandwich structures.

Apart from the tetraphenylborate adducts, there are two other adducts that appear to be of 2/3 stoichiometry, these being adducts formulated as $(CsI)_2 \cdot (CuL_3)_3 \cdot 2H_2O$ and $(NaI)_2 \cdot (NiL_3)_3 \cdot 2H_2O$ (see Experimental Section). The sodium adduct is of particular interest, since the stoichiometry will almost inevitably demand the club sandwich structure. Thus, in this instance the sodium ions are not in the plane of the salicylaldimine oxygens as they were in the sodium nitrate adduct structures described earlier. The fact that a metal ion is of sufficient size to be located in the plane of the Schiff base oxygens does not guarantee that it will do so. For example, whereas magnesium ion is located in the plane of the Schiff base oxygens in the 1/1 adduct of magnesium nitrate with NiL_4, it is sandwiched between two sets of salicylaldimine oxygens in the structure of the 1/2 adduct of magnesium bromide with NiL_4. In this latter structure, electrostatic interactions are with six of the oxygens (three from each salicylaldimine ligand), and presumably this will be the case in the sodium adduct of 2/3 stoichiometry.

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Supporting Information Available: Eight crystallographic files, in CIF format, are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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