Synthesis and Properties of Crown Ether–Alkali Metal Cation Intercalation Compounds of MPS_3 (M = Mn, Cd, Zn)

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Received July 2, 1992

The crown ether-alkali metal cation intercalation compounds (15-crown-5)$_{0.33}$K$_{0.4}$Mn$_{0.8}$PS$_3$ (**4**), (15-crown-5)$_{0.43}$K$_{0.5}$Cd$_{0.75}$PS$_3$·H$_2$O (**5**), (15-crown-5)$_{0.3}$Na$_{0.5}$Zn$_{0.75}$PS$_3$·H$_2$O (**6**), (15-crown-5)$_{0.43}$K$_{0.3}$Na$_{0.2}$Cd$_{0.75}$PS$_3$·H$_2$O (**7a–b**), and the new cationic ionophore [CpRu(benzo-15-crown-5)]PF$_6$ (**1**, Cp = η^5-C$_5$H$_5$) and its derivatives [CpRu(benzo-15-crown-5)]Cl (**2**), [CpRu(benzo-15-crown-5)(NaPF$_6$)]BPh$_4$ (**21**), and [CpRu(benzo-15-crown-5)(NaPF$_6$)]PF$_6$ (**22**) are described. Ion-exchange intercalation of **1** gave [CpRu(benzo-15-crown-5)]$_{0.23}$Na$_{0.4}$Mn$_{0.7}$PS$_3$·H$_2$O (**8**), [CpRu(benzo-15-crown-5)]$_{0.28}$(Me$_4$N)$_{0.02}$Mn$_{0.85}$PS$_3$·H$_2$O (**9**), [CpRu(benzo-15-crown-5)]$_{0.27}$Na$_{0.5}$Cd$_{0.6}$PS$_3$·H$_2$O (**10**), and [CpRu(benzo-15-crown-5)]$_{0.34}$Na$_{0.1}$Zn$_{0.8}$PS$_3$·H$_2$O (**11**). The intercalates [CpFe(C$_6$Me$_6$)]$_{0.28}$Cd$_{0.6}$Na$_{0.5}$PS$_3$·H$_2$O (**12**) and related materials containing [CpRu(p-cymene)]$^+$ (p-cymene = 4-isopropyltoluene), [CpFe(o-C$_6$H$_4$Cl$_2$)]$^+$, and [Cp*Ru(C$_6$H$_6$)]$^+$ (Cp* = η^5-C$_5$Me$_5$) intercalated into MnPS$_3$ and CdPS$_3$ have been prepared, and X-ray powder diffraction suggests that in this series the metal sandwich compounds' principal axes are parallel to the layer planes of the host lattice. Binding of Na$^+$ by **1** in CD$_3$CN and by **2** in D$_2$O has been studied by ^{13}C and ^{23}Na NMR spectroscopy. The crystal structure of **21** [C$_{43}$H$_{45}$BF$_6$NaO$_5$PRu, monoclinic, $P2_1/c$, a = 9.039(1) Å, b = 14.543(1) Å, c = 31.365(4) Å, β = 96.61(1)°, Z = 4, R = 0.042] confirms crown ether–Na$^+$ complexation and includes an unusual η^2-coordination of PF$_6^-$ to the sodium ion. A solid-state ^{23}Na NMR study of intercalates **6**, **7a–b**, and **10–12** suggests that sodium cations in these intercalates exist in several possible environments.

Introduction

Alkali metal cations are common guests in intercalation compounds, and they can often undergo exchange with larger cations to produce new intercalates that cannot be prepared directly from the host compound.[1] We set out to study the interlayer coordination chemistry of Na$^+$ together with crown ethers (host–guest chemistry in a host lattice) in order to investigate both the environment of the intercalated alkali metal cations and the effect of intercalation on the ability of the crown ether to bind sodium ions. It seems possible that intercalation might impose a more rigid conformation on an included crown ether, which might lead to more selective ion binding.

Previous work has described the intercalation of crown ethers and cryptands, sometimes together with alkali metal cations, into layered solids such as FeOCl, graphite, and montmorillonite clay, and some spectroscopic evidence for ion–complexant interaction within the interlayer space has been presented.[2] Here we report the synthesis of intercalates of the layered MPS$_3$ (M = Mn, Cd, Zn) materials containing sodium and potassium cations and crown ethers and their study by ^{23}Na solid-state NMR spectroscopy.[3] Further, we report a comparison of the coordination chemistry of the new organometallic crown ether complex cation [CpRu(η^6-benzo-15-crown-5)]$^+$ (Cp = η^5-C$_5$H$_5$) with Na$^+$ in solution and after intercalation.

Results and Discussion

Choice of Host and Guest. We chose to study the MPS$_3$ (M = Mn, Cd, Zn) compounds as host lattices because they are easy to prepare and they readily intercalate even bulky cations. Thus, Clement and co-workers have shown that MnPS$_3$ and CdPS$_3$ undergo ion-exchange intercalation with guest cations. In these intercalation reactions some of the M^{2+} ions of the host layer are dissociated from the solid into solution and charge balance is maintained by the uptake into the interlayer space of two monocationic guests for each M^{2+} lost (Scheme I).[4] Normally, water molecules are also included into the intercalates and they presumably solvate the cations. Small intercalated cations, such as those of the alkali metals or ammonium salts, can be replaced by ion-exchange with larger guest cations such as metal sandwich complexes.

For purposes of comparison, we have also studied amorphous ZnPS$_3$ as a host lattice. The reaction between Na$_4$P$_2$S$_6$·6H$_2$O and ZnSO$_4$·7H$_2$O in water[5] precipitates a white powder, which, after filtration, washing, and drying in vacuo, analyzes (Zn, H) for ZnPS$_3$·3H$_2$O and exhibits an IR spectrum closely similar to those of the MPS$_3$ compounds prepared at high temperatures.

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Scheme I

$$MPS_3 + A^+ \rightarrow A_{2x}M_{1-x}PS_3$$

$$A_{2x}M_{1-x}PS_3 + G^+ \rightarrow G_yA_{2x-y}M_{1-x}PS_3$$

$$M = Mn, Cd$$

$$A = K, Na, Me_4N$$

$$G = Cp_2Co, CpFe(C_6H_6)$$

This amorphous $ZnPS_3$ material can intercalate bulky cations directly[5a] without requiring preintercalation followed by ion exchange.

As noted above, the intercalation of metallocene and other organometallic sandwich compounds in the MPS_3 phases and in other hosts is well-known.[1] In order to achieve the intercalation of a crown ether system, we have prepared a new sandwich compound which contains the desired ionophore, namely [CpRu(η^6-benzo-15-crown-5)]PF_6 (**1**). Compound **1** was formed from the reaction between [CpRu(NCMe)$_3$]PF_6[6] and benzo-15-crown-5 in hot 1,2-dichloroethane as white crystals in 68% yield. Elution of **1** from a Cl^--loaded ion-exchange column gave water-soluble [CpRu(benzo-15-crown-5)]Cl (**2**) as white crystals after recrystallization from an acetone/ether mixture at −20 °C. The propensity of **2** to crystallize with varying amounts of water precluded satisfactory elemental analyses, but IR spectroscopy confirmed the PF_6 anion had been exchanged. The related compound {CpRu[o-C_6H_4(MeO)$_2$]}PF_6 (**3**) was prepared as a model for **1** (Scheme II) in order to test the thesis that the crown ether portion of **1** was responsible for binding sodium cations. The analytical and spectroscopic data characterizing **1–3** are given in the Experimental Section. The ^1H and ^{13}C NMR spectra of these compounds include signals with characteristic upfield shifts due to the protons and carbons of the complexed arenes.

Scheme II

$$\underset{L = MeCN}{[CpRuL_3]PF_6} + \text{arene} \xrightarrow[\Delta,\ -3L]{\text{arene}} [CpRu(\eta^6\text{-arene})]PF_6$$

arene = benzo-15-crown-5 (**1**)
arene = [o-C_6H_4(OMe)$_2$] (**3**)

$$\underset{\mathbf{1}}{[CpRu(\text{benzo-15-crown-5})]PF_6} \xrightarrow[H_2O]{\text{Dowex–}Cl^-} \underset{\mathbf{2}}{[CpRu(\text{benzo-15-crown-5})]Cl}$$

Crown Ether Intercalates. The MPS_3 intercalation compounds containing alkali metal cations and crown ether guests were prepared in two ways: either by direct reaction of the host with an alkali metal cation and 15-crown-5 or by intercalation of alkali cations followed by ion-exchange intercalation of complex **1**.

As shown in Scheme III, the reaction between MPS_3 and an excess of alkali metal cations and 15-crown-5 in water gives the intercalates (15-crown-5)$_{0.33}K_{0.4}Mn_{0.8}PS_3$ (**4**) and (15-crown-5)$_{0.3}Na_{0.5}Zn_{0.75}PS_3\cdot H_2O$ (**6**). The synthesis of (15-crown-5)$_{0.43}K_{0.5}Cd_{0.75}PS_3\cdot H_2O$ (**5**), as in the direct intercalation of potassium ions in $CdPS_3$, requires addition of a $KHCO_3/K_2CO_3$ buffer and EDTA to complex the dissociated Cd^{2+} ions. We monitored the progress of these reactions by X-ray powder

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Scheme III[a]

$$MPS_3 \xrightarrow{\text{i}} \underset{\mathbf{4}}{(15\text{-crown-5})_{0.33}K_{0.4}Mn_{0.8}PS_3}$$

$$MPS_3 \xrightarrow{\text{ii}} \underset{\mathbf{5}}{(15\text{-crown-5})_{0.3}Na_{0.5}Zn_{0.75}PS_3\cdot H_2O}$$

$$MPS_3 \xrightarrow{\text{iii}} \underset{\mathbf{6}}{(15\text{-crown-5})_{0.43}K_{0.5}Cd_{0.75}PS_3\cdot H_2O} \xrightarrow{\text{ii}} \underset{\mathbf{7}}{(15\text{-crown-5})_{0.43}K_{0.3}Na_{0.2}Cd_{0.75}PS_3\cdot H_2O}$$

[a] Reagents: (i) 15-crown-5, KCl, H_2O; (ii) 15-crown-5, NaCl, H_2O; (iii) 15-crown-5, KCl, $KHCO_3$, K_2CO_3, EDTA, H_2O.

diffraction (XRD) and often observed the known alkali metal cation intercalates as intermediate phases before the final products were formed. The reaction between **5** and an excess of Na^+ in water gave the partially ion-exchanged (15-crown-5)$_{0.43}K_{0.3}Na_{0.2}Cd_{0.75}PS_3\cdot H_2O$ (**7a**); complete exchange of K^+ by Na^+ could not be obtained under these conditions. Attempts at further exchange yielded product **7b**, whose XRD spectrum, elemental analysis, and IR spectrum were indistinguishable from those of **7a**, but which could be distinguished from **7a** by solid-state NMR spectroscopy (see below). An attempt to prepare the fully Na^+-exchanged analogue of **7a** by the reaction between $Na_{0.8}Cd_{0.6}PS_3\cdot 1.5H_2O$ and NaCl and 15-crown-5 in water was also unsuccessful.

Ion-exchange by organometallic cations of intercalated alkali metal and ammonium cations (Scheme IV) was used to prepare the intercalates of ionophore complex **1** and other sandwich cations. These reactions were carried out in acetone–water suspensions at 60–80 °C and were usually complete in a few days, as determined by X-ray powder diffraction data. The reactions were faster for the Mn compounds than the Cd ones, and replacement of alkali metal cations was faster than exchange of ammonium salts. For the amorphous $ZnPS_3$ phase, organo-

Scheme IV

$$MPS_3 \xrightarrow{A^+} A_{2x}M_{1-x}PS_3\cdot bH_2O$$

M = Mn; A = Na, $x = 0.3$, $b = 1$
A = K, $x = 0.2$, $b = 1$
A = Me_4N, $x = 0.15$, $b = 1$

M = Cd; A = Na, $x = 0.4$, $b = 1.5$

M = Zn; A = Na, $x = 0.2$, $b = 1.75$ (**17**)
A = Me_4N, $x = 0.25$, $b = 1$ (**18**)
A = [CpFe(C_6Me_6)], $x = 0.21$, $b = 2$ (**19**)

$$A_{2x}M_{1-x}PS_3\cdot bH_2O \xrightarrow{G^+} \underset{\mathbf{8\text{–}16,\ 20}}{A_{2x-y}G_yM_{1-x}PS_3\cdot cH_2O}$$

[CpRu(benzo-15-crown-5)]$_{0.23}Na_{0.4}Mn_{0.7}PS_3\cdot H_2O$ (**8**)
[CpRu(benzo-15-crown-5)]$_{0.28}Me_4N_{0.02}Mn_{0.85}PS_3\cdot H_2O$ (**9**)
[CpRu(benzo-15-crown-5)]$_{0.27}Na_{0.5}Cd_{0.6}PS_3\cdot H_2O$ (**10**)
[CpRu(benzo-15-crown-5)]$_{0.34}Na_{0.1}Zn_{0.8}PS_3\cdot H_2O$ (**11**)
[CpFe(C_6Me_6)]$_{0.28}Na_{0.5}Cd_{0.6}PS_3\cdot H_2O$ (**12**)
[CpRu(p-cymene)]$_{0.21}Na_{0.4}Mn_{0.7}PS_3\cdot H_2O$ (**13**)
[CpRu(p-cymene)]$_{0.25}Me_4N_{0.05}Mn_{0.85}PS_3\cdot H_2O$ (**14**)
[CpFe(o-$C_6H_4Cl_2$)]$_{0.4}K_{0.02}Mn_{0.8}PS_3\cdot H_2O$ (**15**)
[Cp*Ru(C_6H_6)]$_{0.26}K_{0.1}Mn_{0.8}PS_3\cdot H_2O$ (**16**)
[CpFe(C_6Me_6)]$_{0.39}Na_{0.05}Zn_{0.8}PS_3\cdot 1.5H_2O$ (**20**)

Table I. Analytical and XRD Data for the Intercalates

no.	intercalate	anal. found (calcd)	interlayer spacing, Å
4	$(15\text{-crown-}5)_{0.33}K_{0.4}Mn_{0.8}PS_3$	K, 4.40 (6.03); Mn, 18.5 (16.9); C, 15.1 (15.3); H, 2.59 (2.57)	15.5
5	$(15\text{-crown-}5)_{0.43}K_{0.5}Cd_{0.75}PS_3\cdot H_2O$	K, 3.82 (5.69); Cd, 25.5 (24.5); C, 14.9 (15.0); H, 2.45 (3.11)	15.6
6	$(15\text{-crown-}5)_{0.3}Na_{0.5}Zn_{0.75}PS_3\cdot H_2O$	Na, 4.09 (4.23); Zn, 17.8 (18.0); C, 13.4 (13.3); H, 2.98 (2.97)	amorphous[a]
7	$(15\text{-crown-}5)_{0.43}K_{0.3}Na_{0.2}Cd_{0.75}PS_3\cdot H_2O$	K, 2.37 (3.44); Na, 0.80 (1.35); Cd, 26.2 (24.8); C, 15.1 (15.2); H, 2.64 (3.14)	15.6
8	$[CpRu(benzo\text{-}15\text{-crown-}5)]_{0.23}Na_{0.4}Mn_{0.7}PS_3\cdot H_2O$	Na, 2.18 (3.14); Mn, 14.0 (13.1); C, 18.2 (17.9); H, 2.33 (2.67)	15.2
9	$[CpRu(benzo\text{-}15\text{-crown-}5)]_{0.28}Me_4N_{0.02}Mn_{0.85}PS_3\cdot H_2O$	Mn, 14.6 (14.8); C, 20.8 (20.6); N, 0.20 (0.09); H, 2.43 (2.96)	15.2
10	$[CpRu(benzo\text{-}15\text{-crown-}5)]_{0.27}Na_{0.5}Cd_{0.6}PS_3\cdot H_2O$	Na, 1.8 (3.37); Cd, 20.3 (18.0); C, 17.9 (18.0); H, 2.1 (2.59)	15.2
11	$[CpRu(benzo\text{-}15\text{-crown-}5)]_{0.34}Na_{0.1}Zn_{0.8}PS_3\cdot H_2O$	Na, 0.80 (0.66); Zn, 14.4 (15.0); C, 22.5 (22.3); H, 2.70 (3.05)	a
12	$[CpFe(C_6Me_6)]_{0.28}Na_{0.5}Cd_{0.6}PS_3\cdot H_2O$	Na, 1.1 (3.79); Fe, 5.9 (5.15); Cd, 22.9 (22.2); C, 18.9 (18.8); H, 2.47 (2.81)	13.5
13	$[CpRu(p\text{-cymene})]_{0.21}Na_{0.4}Mn_{0.7}PS_3\cdot H_2O$	Na, 3.1 (3.60); Mn, 15.5 (15.0); C, 14.9 (14.8); H, 1.8 (2.36)	12.2
14	$[CpRu(p\text{-cymene})]_{0.25}Me_4N_{0.05}Mn_{0.85}PS_3\cdot H_2O$	Mn, 18.3 (17.3); C, 18.0 (17.5); H, 2.08 (2.74); N, 0.32 (0.26)	12.2
15	$[CpFe(o\text{-}C_6H_4Cl_2)]_{0.4}K_{0.02}Mn_{0.8}PS_3\cdot H_2O$	K, 0.31 (0.26); Cl, 6.50 (9.5); Fe, 8.72 (7.5); Mn, 14.7 (14.8); C, 17.7 (17.8); H, 1.43 (1.90)	12.6
16	$[Cp^*Ru(C_6H_6)]_{0.26}K_{0.1}Mn_{0.8}PS_3\cdot H_2O$	K, 0.13 (1.42); Mn, 18.8 (16.0); C, 18.3 (18.2); H, 2.1 (2.74)	13.6
17	$Na_{0.4}Zn_{0.8}PS_3\cdot 1.75H_2O$	Na, 4.44 (4.18); Zn, 24.0 (23.8); H, 1.77 (1.59)	a
18	$Me_4N_{0.5}Zn_{0.75}PS_3\cdot H_2O$	Zn, 21.8 (21.2); C, 10.6 (10.4); N, 2.93 (3.02); H, 3.16 (3.46)	a
19	$[CpFe(C_6Me_6)]_{0.42}Zn_{0.8}PS_3\cdot 2H_2O$	Zn, 15.1 (15.6); Fe, 8.51 (7.01); C, 25.6 (25.6); H, 3.31 (4.12)	a
20	$[CpFe(C_6Me_6)]_{0.39}Na_{0.05}Zn_{0.8}PS_3\cdot 1.5H_2O$	Na, 0.20 (0.36); Zn, 15.7 (16.4); Fe, 6.40 (6.85); C, 24.8 (25.0); H, 3.20 (3.80)	a

[a] Not available.

metallic cations were either directly intercalated or ion exchanged with the intercalated Na^+ cations of $Na_{0.4}Zn_{0.8}PS_3\cdot 1.75H_2O$.

The new intercalates **4–20** were characterized by elemental analysis, XRD, and IR spectroscopy. Compound **10** was also characterized by solid-state ^{13}C NMR spectroscopy (see Experimental Section). In most cases elemental analyses were consistent with the stoichiometry required for charge balance (two monocationic guests taken up per M^{2+} lost). They also demonstrate that variable amounts of water are associated with the intercalates. XRD (for Mn and Cd compounds) was used to monitor the reactions and to ensure that they reached completion and yielded single-phase materials. Typically the spectrum of the starting material disappeared and was replaced by a new series of $00l$ lines due to the product; from these the new interlayer distance in the intercalate could be calculated, within an estimated experimental error of 0.2 Å. In a few cases some $h00$ and $0k0$ lines (assigned by assuming little change in the host lattice a and b distances on intercalation) were also observed, as reported in the Experimental Section. The $ZnPS_3$ intercalates were amorphous to X-rays, and it was impossible to show that they were single phases. These materials could, however, be characterized by elemental analysis. Analytical data and interlayer distances (when available) for the new intercalates prepared in this work are given in Table I.

The infrared spectra of the new intercalates are reported in the experimental section. They show, inter alia, bands corresponding to those of the free neutral and cationic guests. As previously observed, intercalation also caused a splitting of the low-energy MPS_3 P–S band into two peaks.[7] This effect was not observed, however, for the $ZnPS_3$ materials, presumably because of their amorphous nature.

The $MnPS_3$ intercalate **9** containing both Me_4N^+ and the cation of crown ether complex **1** was prepared in the expectation that it would undergo ion uptake of Na^+ from solution, by preferential exchange of the intercalated ammonium cation. Treatment of **9** with aqueous Na^+ gave a product whose XRD spectrum was indistinguishable from the starting material, even though elemental analysis suggested loss of Me_4N and uptake of Na. Since **9** contains only a small amount of Me_4N^+, however, the compositional changes observed are about the same size as the errors inherent in the elemental analyses.

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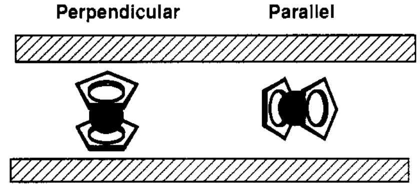

Figure 1. Two possible extreme orientations with respect to the layers for intercalated metallocenes (or metal sandwich complexes).

Guest Orientation inside the Layers. We have studied the geometry of the intercalated organometallic sandwiches using XRD. Previous work had shown that such guest compounds can adopt two extreme orientations in which the principal axis of the "metallocene" may be parallel or perpendicular to the host layers, as shown in Figure 1.[8] The interlayer distance found for the intercalates **8–10** and **12–16** (Table I) correlates well with the size of the arene ring of the guest cations, so these data suggest that the intercalated sandwich cations adopt the parallel orientation, as illustrated in Figure 2.

The data in Table I also show that the interlayer distance (d) depends, as expected, on the size of the largest guest cation. Thus the intercalates **13–14** containing $[CpRu(p\text{-cymene})]^+$ (p-cymene = 4-isopropyltoluene) and either Na^+ or Me_4N^+ guests have the same interlayer spacing (direct comparison of $MnPS_3$ and $CdPS_3$ intercalates is possible since the prinstine hosts have the same interlayer spacing, within our experimental error). Further, these intercalates have the same d value, within experimental error, as that (12.08 ± 0.03 Å) reported for $Mn_{0.85}[CpFe(C_6H_6)]_{0.3}PS_3$,[9] which suggests that the p-isopropyl and methyl groups are arranged as shown in Figure 2 so that they do not push the layers apart. In accord with this hypothesis, the intercalate (**15**) of $[CpFe(o\text{-}C_6H_4Cl_2)]^+$, in which the guest cannot be oriented so as to avoid this contact with the host layers, has an increased d spacing. Similarly, increasing the size of the arene ring as in the guest $[CpFe(C_6Me_6)]^+$ (compound **12**) or the size of the Cp ring as in $[Cp^*Ru(C_6H_6)]^+$ (**16**, $Cp^* = \eta^5\text{-}C_5Me_5$) also leads to an increase in the interlayer distance. Within experimental error the same d spacing is found for these intercalates, which is consistent with their guests having approximately equal dimen-

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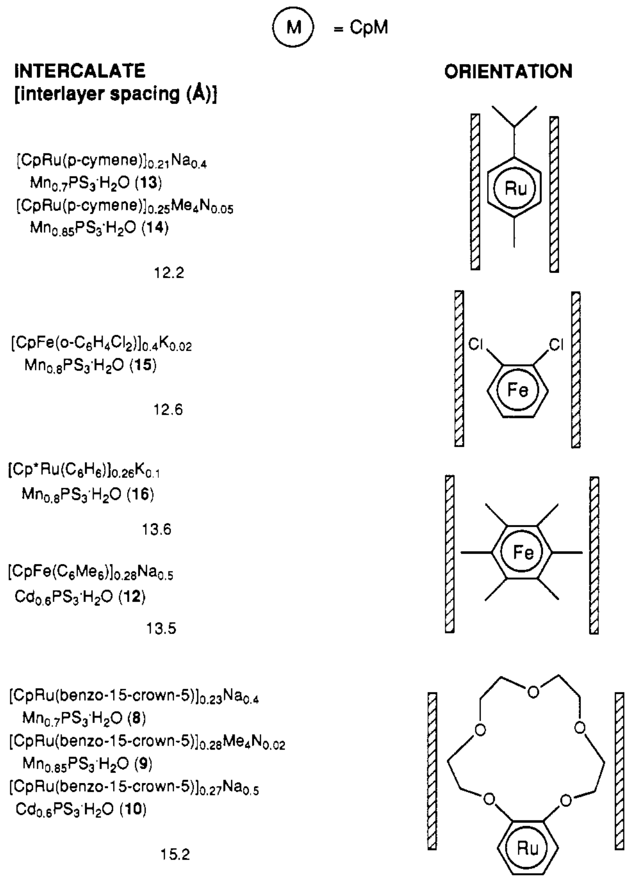

Figure 2. Interlayer distances (±0.2 Å) and proposed guest orientations for $MnPS_3$ and $CdPS_3$ intercalates.

sions.[10] The *d* spacing observed in the intercalates of $[CpRu(benzo\text{-}15\text{-}crown\text{-}5)]^+$ (**8–10**) is also consistent with the parallel orientation shown in Figure 2. The observed increase in interlayer spacing from $Mn_{0.85}[CpFe(C_6H_6)]_{0.3}PS_3$ to **8–10** reflects the larger "width" (ca. 3 Å), in the conformation shown, of benzo-15-crown-5 in comparison with benzene. Rotation of the arene ring in **8–10** by 90° would produce an even larger (by ca. 1.5 Å) interlayer spacing than the one observed.

We note that the *d* spacing refers only to extremes and it is possible that only a relatively small number of guest molecules are aligned parallel and prop up the layers while other guests adopt a range of orientations between the layers. Thus the interlayer spacing alone may not necessarily reflect the orientation of all intercalated cations. Information on this question has been obtained in simpler cases by solving the one-dimensional crystal structure of an intercalate.[11] The relatively low symmetry and complexity of the guest molecules in the materials reported here would preclude definitive analysis by this method.

Sodium Ion Binding in Solution by 1. In order to compare the ion-binding properties of crown ether complex **1** in solution and in the intercalation compounds we first examined the solution chemistry. Binding of Na^+ by **1** in CD_3CN was studied by titrations monitored by ^{13}C and by ^{23}Na NMR spectroscopy. Addition of aliquots of $NaBPh_4$ in CD_3CN to a CD_3CN solution of **1** caused chemical shift changes of the four signals due to the

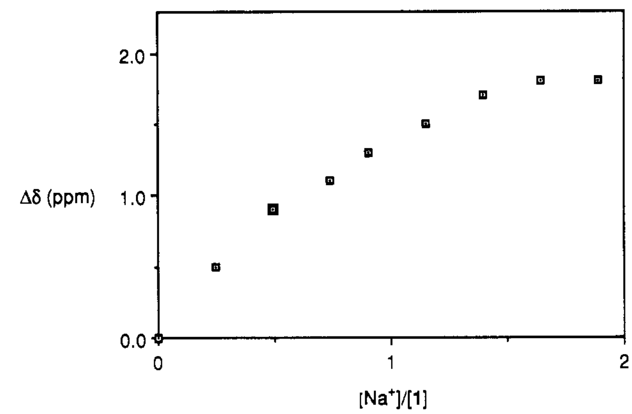

Figure 3. Titration curve for the reaction of $[CpRu(benzo\text{-}15\text{-}crown\text{-}5)]PF_6$ (**1**) with $NaBPh_4$ in CD_3CN as monitored by ^{13}C NMR spectroscopy.

crown ether methylene carbons, as has been observed for other related ionophores upon alkali metal cation binding.[12] Plotting the change in chemical shift for one of these carbons vs. the ratio of concentrations $[Na^+]/[\mathbf{1}]$ gives the titration curve shown in Figure 3. This graph provides good evidence for the binding of the sodium ion by the crown ether under these conditions. Ideally, the titration curve should level off at the complexant:guest ratio of 1.[12] The observed nonideality of the experimental data is caused by the fact that the crown ether complex **1** is cationic and therefore less effective than a neutral complexant and also by the use of the relatively polar solvent acetonitrile, which competes with the crown ether for solvation of the sodium ion. As a control, the model complex $\{CpRu[o\text{-}C_6H_4(MeO)_2]\}PF_6$ (**3**) was titrated with $NaBPh_4$ under identical conditions. In this case, and as expected, no changes in the ^{13}C spectrum of **3** were observed.

Similar titration curves were obtained when a companion experiment was monitored by ^{23}Na NMR spectroscopy.[13] Thus, addition of aliquots of complex **1** in acetonitrile-d_3 to a CD_3CN solution of $NaBPh_4$ causes changes in the ^{23}Na chemical shift, and increases in the line width of the signal, as reported for titrations involving other complexants.[14] The resulting titration curves (Figure 4) closely resemble those obtained from the ^{13}C NMR study and provide further evidence for complexation of Na^+ by **1** in acetonitrile solution.

Titration of **2** with NaCl in D_2O was monitored by ^{13}C NMR spectroscopy as described above, but in this case no changes in the carbon chemical shifts of **2** were observed. This result suggests that the cationic complexant $CpRu(benzo\text{-}15\text{-}crown\text{-}5)^+$ does not bind Na^+ efficiently in competition with water ligands in aqueous solution. This observation was expected since even neutral crown ethers bind sodium cations poorly in water.[15]

Scheme V

$$[CpRu(benzo\text{-}15\text{-}crown\text{-}5)]PF_6\ (\mathbf{1}) \xrightarrow{NaX} [CpRu(benzo\text{-}15\text{-}crown\text{-}5)]PF_6\cdot NaX$$

$$X = BPh_4\ (\mathbf{21})$$
$$X = PF_6\ (\mathbf{22})$$

Further evidence for the ability of **1** to bind sodium cations was provided by the isolation of the Na^+–crown ether complex $[CpRu(benzo\text{-}15\text{-}crown\text{-}5)(NaPF_6)]BPh_4$ (**21**) from the titrations in acetonitrile; $[CpRu(benzo\text{-}15\text{-}crown\text{-}5)(NaPF_6)]PF_6$ (**22**) was

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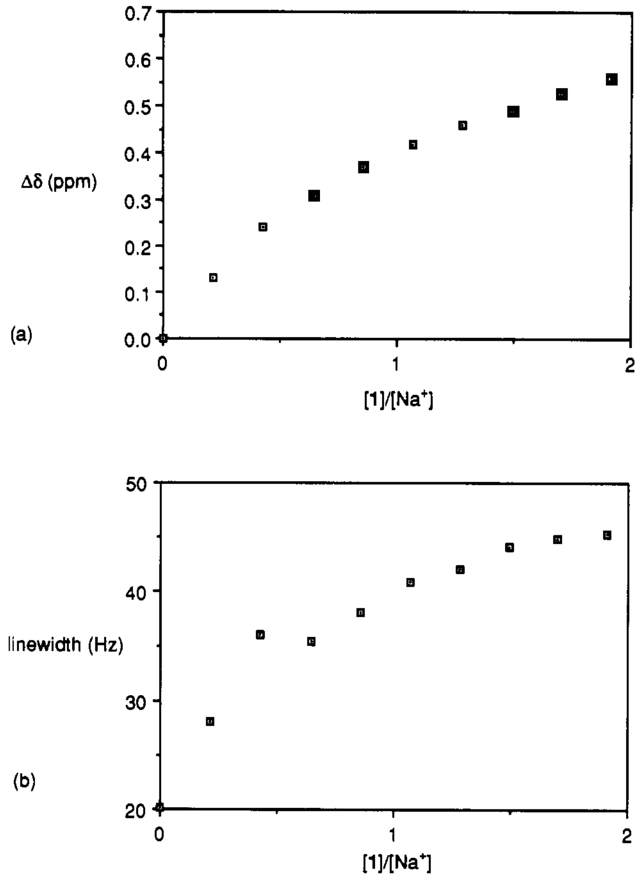

Figure 4. Titration curves for the reaction of [CpRu(benzo-15-crown-5)]PF_6 (**1**) with $NaBPh_4$ in CD_3CN as monitored by ^{23}Na NMR spectroscopy: (a) change in ^{23}Na chemical shift; (b) change in ^{23}Na line width.

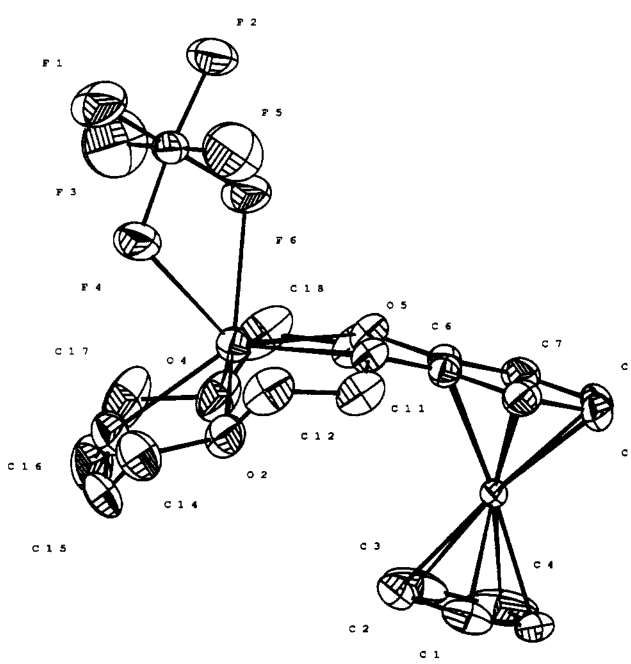

Figure 5. ORTEP drawing of the cation of [CpRu(benzo-15-crown-5)($NaPF_6$)]BPh_4 (**21**).

prepared similarly (Scheme V). The sodium tetraphenylborate complex **21** was recrystallized from acetone/ether at −20 °C to give X-ray quality white crystals. The crystal structure was determined by standard methods and the data refined to an R value of 4.2%. An ORTEP diagram of the cation is shown in Figure 5 and Tables II–V give data collection and refinement parameters, refined atomic coordinates and thermal parameters, and selected bond lengths and angles.

Table II. Crystallographic Data for [CpRu(benzo-15-crown-5)($NaPF_6$)]BPh_4 (**21**)

formula	$C_{43}H_{45}BF_6NaO_5PRu$	Z	4
fw	921.66	temp, °C	20
space group	$P2_1/c$ (No. 14)	radiation (λ, Å)	Cu Kα (1.5418)
a, Å	9.039(1)	D_c, g cm^{-3}	1.49
b, Å	14.543(1)	μ, cm^{-1}	4.927
c, Å	31.365(4)	R^a	0.042
β, deg	96.61(1)	$R_w{}^b$	0.050
cell vol, Å^3	4095.5		

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = \{\sum(|F_o| - |F_c|)^2/\sum|F_o|^2\}^{1/2}$.

Table III. Fractional Atomic Coordinates for the Cation of [CpRu(benzo-15-crown-5)($NaPF_6$)]BPh_4 (**21**)

atom	x/a	y/b	z/c	$U_{equiv}{}^a$
Ru(1)	0.35314(3)	0.11196(2)	0.152885(8)	0.0362
C(1)	0.5677(5)	0.1529(4)	0.1337(2)	0.0647
C(2)	0.4813(5)	0.2293(3)	0.1352(2)	0.0647
C(3)	0.4472(7)	0.2408(5)	0.1755(3)	0.0794
C(4)	0.5118(8)	0.1709(8)	0.2012(2)	0.0865
C(5)	0.5880(5)	0.1154(4)	0.1754(3)	0.0748
C(6)	0.1049(4)	0.1274(3)	0.1407(1)	0.0454
C(7)	0.1422(5)	0.0780(4)	0.1794(1)	0.0596
C(8)	0.2318(5)	−0.0013(4)	0.1798(2)	0.0650
C(9)	0.2831(6)	−0.0323(3)	0.1423(2)	0.0655
C(10)	0.2483(5)	0.0161(3)	0.1039(2)	0.0600
C(11)	0.1583(4)	0.0961(2)	0.1026(1)	0.0454
C(12)	0.2091(5)	0.1347(4)	0.0318(1)	0.0615
C(13)	0.1784(6)	0.2118(4)	0.0020(1)	0.0758
C(14)	0.2121(8)	0.3736(5)	0.0036(3)	0.0985
C(15)	0.2319(8)	0.4491(5)	0.0340(3)	0.0969
C(16)	0.118(1)	0.5077(4)	0.0949(3)	0.1095
C(17)	0.003(1)	0.4803(5)	0.1239(3)	0.0943
C(18)	−0.0653(7)	0.3448(5)	0.1618(2)	0.0796
C(19)	−0.0020(6)	0.2525(4)	0.1759(1)	0.0665
O(1)	0.1191(3)	0.1464(2)	0.06680(8)	0.0456
O(2)	0.2076(4)	0.2930(3)	0.0274(1)	0.0709
O(3)	0.1069(5)	0.4497(2)	0.06002(2)	0.0883
O(4)	0.0382(5)	0.3876(2)	0.1377(1)	0.0796
O(5)	0.0191(3)	0.2035(2)	0.13700(8)	0.0495
Na(1)	0.0161(2)	0.3022(1)	0.07216(5)	0.0513
P(1)	−0.3130(1)	0.28468(9)	0.02035(4)	0.0585
F(1)	−0.3895(4)	0.3170(3)	−0.0237(1)	0.1082
F(2)	−0.4502(3)	0.2241(3)	0.0281(1)	0.0890
F(3)	−0.3722(7)	0.3655(4)	0.0424(2)	0.1568
F(4)	−0.1639(4)	0.3349(3)	0.0117(1)	0.0949
F(5)	−0.2492(5)	0.1956(3)	−0.0022(2)	0.1383
F(6)	−0.2283(3)	0.2475(3)	0.0642(1)	0.0906

^{a} $U_{equiv} = [\prod_{i=1}^{3} U_i]^{1/3}$ where u_i = principal axis (Å^2) of ellipse.

The cation of **21** consists of the CpRu–arene sandwich, with the crown ether–Na^+ portion bent away from the benzene ring with a hinge angle of 36°. The sodium cation is bound by the five crown ether oxygens (Na–O distances range from 2.344(4) to 2.487(4) Å), and the Na^+ is displaced from the best plane of the five oxygens by 0.81 Å.

The sodium cation is also bound to two of the fluorines of the PF_6 anion, giving seven-coordinate sodium. Although the PF_6 anion rarely acts as a ligand, this coordination mode has been described previously for example in the structure of (15-crown-5)$NaPF_6$.[16] The Na–F distances of 2.400(4) Å and 2.334(3) Å in **21** may be compared to those found in this simpler compound [2.46(2) and 2.40(2) Å] or to those in NaF (2.307 Å) and $NaPF_6$ (2.34 Å).[17] Such Na–F interactions reflect the importance of electrostatic considerations in sodium coordination chemistry.[18]

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Table IV. Selected Bond Lengths (Å) for $[CpRu(benzo\text{-}15\text{-}crown\text{-}5)(NaPF_6)]BPh_4$ (**21**)

Ru(1)–C(1)	2.178(4)	Ru(1)–C(2)	2.170(4)
Ru(1)–C(3)	2.144(5)	Ru(1)–C(4)	2.142(5)
Ru(1)–C(5)	2.159(5)	Ru(1)–C(6)	2.244(3)
Ru(1)–C(7)	2.222(4)	Ru(1)–C(8)	2.200(4)
Ru(1)–C(9)	2.206(4)	Ru(1)–C(10)	2.206(4)
Ru(1)–C(11)	2.237(3)	C(1)–C(2)	1.362(7)
C(1)–C(5)	1.408(8)	C(2)–C(3)	1.345(9)
C(3)–C(4)	1.39(1)	C(4)–C(5)	1.38(1)
C(6)–C(7)	1.419(6)	C(6)–C(11)	1.414(5)
C(6)–O(5)	1.348(4)	C(7)–C(8)	1.409(7)
C(8)–C(9)	1.387(8)	C(9)–C(10)	1.400(7)
C(10)–C(11)	1.417(6)	C(11)–O(1)	1.353(4)
C(12)–C(13)	1.464(7)	C(12)–O(1)	1.450(5)
C(13)–O(2)	1.431(7)	C(14)–C(15)	1.45(1)
C(14)–O(2)	1.393(7)	C(15)–O(3)	1.467(9)
C(16)–C(17)	1.51(1)	C(16)–O(3)	1.378(9)
C(17)–O(4)	1.440(8)	C(18)–C(19)	1.506(8)
C(18)–O(4)	1.412(8)	C(19)–O(5)	1.446(5)
O(1)–Na(1)	2.463(3)	O(2)–Na(1)	2.355(4)
O(3)–Na(1)	2.344(4)	O(4)–Na(1)	2.391(4)
O(5)–Na(1)	2.487(3)		
Na(1)–F(4)	2.400(4)	Na(1)–F(6)	2.334(3)
P(1)–F(1)	1.546(3)	P(1)–F(2)	1.562(3)
P(1)–F(3)	1.493(5)	P(1)–F(4)	1.584(3)
P(1)–F(5)	1.614(5)	P(1)–F(6)	1.590(3)

Table V. Selected Bond Angles (deg) for $[CpRu(benzo\text{-}15\text{-}crown\text{-}5)(NaPF_6)]BPh_4$ (**21**)

O(1)–C(11)–C(6)	116.4(3)	O(1)–C(11)–C(10)	124.2(4)
O(1)–C(12)–C(13)	108.1(4)	O(2)–C(13)–C(12)	105.6(4)
O(2)–C(14)–C(15)	107.1(6)	O(3)–C(15)–C(14)	108.9(5)
O(3)–C(16)–C(17)	108.9(6)	O(4)–C(17)–C(16)	106.5(6)
O(4)–C(18)–C(19)	107.4(4)	O(5)–C(19)–C(18)	105.8(4)
C(12)–O(1)–C(11)	116.7(3)	Na(1)–O(1)–C(11)	120.4(2)
Na(1)–O(1)–C(12)	114.1(3)	C(14)–O(2)–C(13)	114.4(5)
Na(1)–O(2)–C(13)	106.1(3)	Na(1)–O(2)–C(14)	109.9(4)
C(16)–O(3)–C(15)	117.1(6)	Na(1)–O(3)–C(15)	113.1(4)
Na(1)–O(3)–C(16)	115.2(5)	C(18)–O(4)–C(17)	115.9(6)
Na(1)–O(4)–C(17)	103.5(4)	Na(1)–O(4)–C(18)	103.6(3)
C(19)–O(5)–C(6)	117.6(3)	Na(1)–O(5)–C(6)	119.7(2)
Na(1)–O(5)–C(19)	114.6(3)	O(2)–Na(1)–O(1)	66.3(1)
O(3)–Na(1)–O(1)	133.5(1)	O(3)–Na(1)–O(2)	70.1(2)
O(4)–Na(1)–O(1)	122.8(1)	O(4)–Na(1)–O(2)	123.2(2)
O(4)–Na(1)–O(3)	70.6(2)	O(5)–Na(1)–O(1)	63.64(9)
O(5)–Na(1)–O(2)	121.0(1)	O(5)–Na(1)–O(3)	133.7(1)
O(5)–Na(1)–O(4)	66.7(1)	F(4)–Na(1)–O(1)	110.8(1)
F(4)–Na(1)–O(2)	91.0(1)	F(4)–Na(1)–O(3)	84.7(1)
F(4)–Na(1)–O(4)	124.0(2)	F(4)–Na(1)–O(5)	134.7(1)
F(4)–Na(1)–P(1)	28.02(8)	F(6)–Na(1)–O(1)	92.3(1)
F(6)–Na(1)–O(2)	131.9(2)	F(6)–Na(1)–O(3)	129.7(2)
F(6)–Na(1)–O(4)	104.7(2)	F(6)–Na(1)–O(5)	79.2(1)
F(6)–Na(1)–F(4)	55.7(1)	F(4)–P(1)–F(1)	90.5(2)
F(3)–P(1)–F(1)	91.6(3)	F(3)–P(1)–F(2)	92.2(3)
F(4)–P(1)–F(2)	173.2(2)	F(4)–P(1)–F(3)	94.2(3)
F(5)–P(1)–F(1)	89.8(3)	F(5)–P(1)–F(4)	86.6(3)
F(5)–P(1)–F(2)	86.9(2)	F(5)–P(1)–F(3)	178.4(3)
F(6)–P(1)–F(1)	176.6(3)	F(6)–P(1)–F(2)	89.2(2)
F(6)–P(1)–F(3)	91.7(3)	F(6)–P(1)–F(4)	88.3(2)
F(6)–P(1)–F(5)	86.9(3)	P(1)–F(4)–Na(1)	106.6(2)
P(1)–F(6)–Na(1)	109.4(2)		

Solid-State ^{23}Na NMR Studies on MPS_3 Intercalates. We have studied the sodium cation environments in the diamagnetic $CdPS_3$ and $ZnPS_3$ intercalates using solid-state ^{23}Na NMR. The ^{23}Na spectra at 9.4 T of four $CdPS_3$ intercalates including the known $Na_{0.8}Cd_{0.6}PS_3{\cdot}1.5H_2O$, the new crown ether intercalates **7a–b**, and the organometallic sandwich intercalates **10** and **12** are shown in Figure 6.

To gauge the relative contribution of chemical shift and quadrupolar effects to the observed chemical shifts, we obtained spectra of the compounds $Na_4P_2S_6{\cdot}6H_2O$ (**22**) and the intercalates **6**, **7b**, and **17** at two different fields, at 9.4 and 4.7 T. The spectrum of **7b** is shown in Figure 7 and is typical of the results. The observed shifts change by less than 3 ppm on halving the field. Since the second-order quadrupole interaction which leads to contribution to the shifts scales with inverse field, this result indicates that shifts measured from the higher field spectrum can only differ from the true chemical shifts by less than 1 ppm in this case. This indicates that meaningful assignments can be made on the basis of the observed chemical shifts at the higher field. Greatly improved resolution is also seen at the higher field, with the line widths scaling approximately as inverse field, indicating that they result predominantly from a second order quadrupolar interaction. Resolved second-order line shapes are not observed, presumably because there is a range of different sites experiencing different quadrupole interactions.

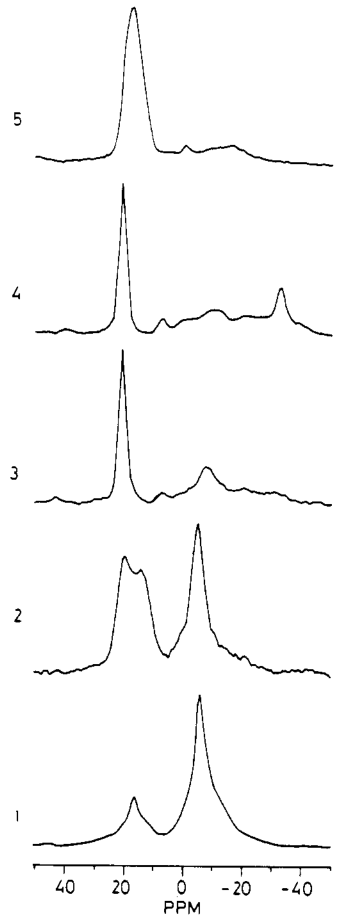

Figure 6. Solid-state ^{23}Na NMR spectra of $CdPS_3$ intercalates. An exponential line broadening of 100 Hz has been applied for all these spectra, and spinning speeds (in Hz) are as noted. Key: (1) $Na_{0.8}Cd_{0.6}PS_3{\cdot}1.5H_2O$, $R\phi$ = 3500; (2) $[CpFe(C_6Me_6)]_{0.28}Na_{0.5}Cd_{0.6}PS_3{\cdot}H_2O$ (**12**), $R\phi$ = 3500; (3 and 4) $[15\text{-}crown\text{-}5]_{0.43}K_{0.3}Na_{0.2}Cd_{0.75}PS_3{\cdot}H_2O$ (**7a–b**), $R\phi$ = 3000 (**7a**), $R\phi$ = 2400 (**7b**); (5) $[CpRu(benzo\text{-}15\text{-}crown\text{-}5)]_{0.27}Na_{0.5}Cd_{0.6}PS_3{\cdot}H_2O$ (**10**), $R\phi$ = 3500.

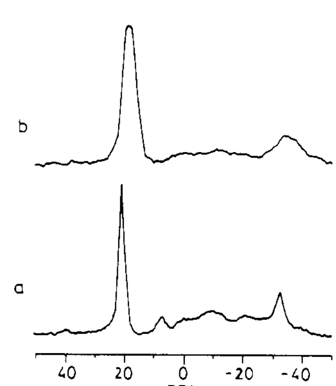

Figure 7. Solid-state ^{23}Na NMR spectra of $[15\text{-}crown\text{-}5]_{0.43}K_{0.3}Na_{0.2}Cd_{0.75}PS_3{\cdot}H_2O$ (**7b**), $R\phi$ = 3500, at different magnetic fields: (a) 9.4 T (b) 4.7 T.

We also carried out some variable-temperature NMR exper-

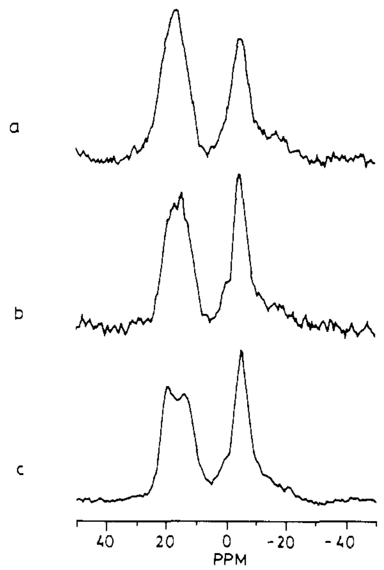

Figure 8. Variable-temperature solid-state ^{23}Na NMR spectra of $[CpFe(C_6Me_6)]_{0.28}Na_{0.5}Cd_{0.6}PS_3{\cdot}H_2O$ (**12**), $R\phi = 3500$: (a) 210 K; (b) 245 K; (c) 298 K.

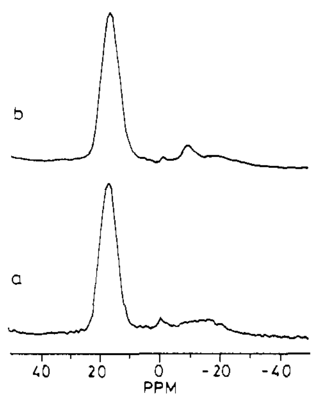

Figure 9. Solid-state ^{23}Na NMR spectra of $[CpRu(benzo\text{-}15\text{-}crown\text{-}5)]_{0.27}Na_{0.5}Cd_{0.6}PS_3{\cdot}H_2O$ (**10**): (a) compound as prepared, $R\phi = 3500$; (b) compound after heating in vacuo, $R\phi = 3700$.

iments on compounds **10–12**. In general, heating or cooling the intercalates caused only small changes in the observed spectra (see Figure 8). Preliminary experiments showed that the water content of the intercalates affected their NMR spectra, as expected from related literature studies of ^{23}Na solid-state chemical shifts.[19] For example, heating a sample of **10** in vacuo, followed by preparing the NMR sample in a glovebox, gave the spectrum shown in Figure 9. However, it proved difficult to prepare samples with reproducible water contents by similar drying and wetting cycles. Therefore, the intercalates were studied as prepared. Typically, samples gave reproducible spectra, even after months of storage in air.

Since sodium is a quadrupolar nucleus, the observed "chemical shifts" are a combination of the isotropic chemical shift and a quadrupolar contribution.[13] Only a few compounds have been studied by solid-state ^{23}Na NMR; however, it appears that the observed "chemical shifts" can be correlated with the sodium ligand environments.[20] For example, molecular hydrates or hydrated sodium in a variety of environments, e.g. zeolites, give rise to "chemical shifts" in the range −3 to −19 ppm, while Na^+–crown ether compounds give rise to shifts in the range −19 to −32

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(20) See ref 3 and (a) Tabeta, R.; Aida, M.; Saito, H. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1957. (b) Turoscy, R.; Leidheiser, Jr., H.; Roberts, J. E. *J. Electrochem. Soc.* **1990**, *137*, 1785. (c) Ellaboudy, A.; Dye, J. L. *J. Magn. Reson.* **1986**, *66*, 491. (d) Aranda, P.; Ruiz-Hitzky, E. *Chem. Mater.* **1992**, *4*, 1395–1404.

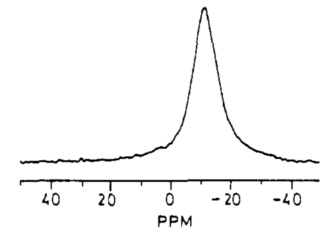

Figure 10. Solid-state ^{23}Na NMR spectrum of $Na_{0.4}Zn_{0.8}PS_3{\cdot}1.75H_2O$ (**17**), $R\phi = 1670$.

ppm. Very recently, the chemical shift of Na^+–hectorite containing intercalated dibenzo-24-crown-8 was reported to be −10.3 ppm.[20d]

Use of such a correlation and data from the ^{23}Na spectra of model compounds, together with other chemical information about the $CdPS_3$ intercalates, enables a qualified assignment of the spectral peaks. For example, we assign the spectrum of $Na_{0.8}Cd_{0.6}PS_3{\cdot}1.5H_2O$ (spectrum 1, Figure 6) as follows. The peak at −8 ppm, in the "hydrate" range, may be assigned to interlayer sodium ligated by water, whose presence is known from analytical and IR data, and this is consistent with the increased interlayer spacing on intercalation. The solid-state ^{23}Na NMR spectrum of the model compound $Na_4P_2S_6{\cdot}6H_2O$ (hydrated sodium in a similar material) shows a broad peak centered at about −4 ppm, consistent with this assignment. The peak at the unusual positive ^{23}Na chemical shift of 18 ppm (Na_2S has been reported to have a chemical shift of 42.5 ppm[3c]) may be assigned to Na^+ occupying Cd^{2+} vacancies in the layers and bound by $P_2S_6^{4-}$ ligands of the host lattice, as suggested by an earlier Raman study[21] of this material. Another possible assignment for this signal is to interlayer sodium bound to surface "sulfide" of the thiophosphate groups in the $CdPS_3$ layer and not exchanging rapidly with other interlayer sodiums. The spectrum of **12** (spectrum 2, Figure 6) can be assigned in the same way, assuming that the addition of the iron sandwich cation does not significantly perturb these two sodium binding sites.

We obtained spectra (spectra 3 and 4, Figure 6) for two different samples containing Na^+ cations and 15-crown-5 (**7a–b**). As noted earlier, compound **7a** was prepared by partial exchange of intercalated K^+ for Na^+, and attempts to cause further exchange gave **7b**. These materials gave rise to different solid-state ^{23}Na NMR spectra. In both spectra, one peak, at about 22 ppm, may again be assigned to a Na^+ located at a "sulfide" site in the host layer. The other signals in these spectra are presumably due to Na^+ interacting in some manner with water molecules and crown ether ligands. We assign the peak at −32 ppm in the spectrum of **7b** to a Na^+–crown ether complex, consistent with the literature shift range and the spectrum of the model complex **22** (broad peak centered at −26 ppm). The remaining broad peaks (0 to −30 ppm) may be due to incomplete chelation of Na^+ ions by the crown ether. These assignments suggest that **7a** differs from **7b** by the extent of Na^+–crown ether interaction. Thus, initial exchange of K^+ may give **7a**, in which the remaining K^+ is bound by crown ether while intercalated Na^+ occurs in sulfide and water sites; further attempts at ion-exchange effect ligand exchange inside the intercalate to give **7b**.

Similar arguments may be used to assign the signals in the spectrum of **10** (spectrum 5, Figure 6) to a large sulfide-site peak and a small broad peak at −15 ppm due to sodium ions complexed by crown ether and water ligands. The integrated intensities of the ^{23}Na NMR peaks in the spectra suggest that Na^+ ions are bound more effectively in competition with other sites by the neutral crown ether in **7a–b** than by the cationic Ru–crown ether complex in **10**, as expected on electrostatic grounds. As discussed previously, the crown ether portion of the intercalated cation of **1** appears to hold apart the layer planes of the host lattice. The

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resulting compression of the ether ring may also contribute to its ineffective binding of sodium cations.

We carried out related NMR studies on the amorphous $ZnPS_3$ materials. Compounds **6**, **11**, **17**, and **20** were examined, but in all cases only one broad ^{23}Na signal could be seen, at varying chemical shifts, as reported in the experimental section. The spectrum of **17**, shown in Figure 10, is typical. The spectra measured at low temperature were similar, as were those obtained at lower field. These results could reflect the amorphous nature of these materials, which are perhaps better described as solid solutions rather than intercalates, or there may be rapid exchange on the NMR time scale between different Na^+ sites.

Conclusions

We have described a series of new intercalates of the layered compounds MPS_3 (M = Mn, Cd, Zn) containing alkali metal cations and crown ethers. Powder diffraction studies of $MnPS_3$ and $CdPS_3$ intercalates of the new ionophore [CpRu(benzo-15-crown-5)]$^+$ and related organometallic sandwich cations suggest that the principal axis of the guest "metallocene" moiety lies parallel to the host lattice planes.

The intercalated sodium cations in the new intercalates can be thought of as guests with a choice of host environments. Solid-state ^{23}Na NMR studies of the $CdPS_3$ intercalates suggest that intercalated Na^+ exists in several different sites, and we propose that these include the Cd^{2+} vacancies in the layers, where it is bound by $P_2S_6^{4-}$ ligands of the host, and the interlayer space, where it interacts with water and/or crown ether ligands.

Our observations confirm that the interlayer environment of the MPS_3 materials is quite unlike organic solutions. The guest cations exist in a polar, aqueous environment, surrounded by negatively charged layers. Under these conditions it is unsurprising that the cationic crown ether complex **1**, which binds sodium cations in acetonitrile, is a less efficient complexant when intercalated due to competition with anionic ($P_2S_6^{4-}$ host layer) and polar neutral (water) ligands, in addition to possible compression and deformation of the crown ether ring by the host lattice layer planes. In contrast, the intercalated neutral crown ether in **7a–b** appears to be a more effective ionophore.

Experimental Section

The following compounds were prepared by literature methods: [CpRu(*p*-cymene)]PF_6,[22] [CpRu(NCMe)$_3$]PF_6,[6] [Cp*Ru(C_6H_6)]PF_6,[10a] [CpFe(C_6Me_6)]PF_6,[23] [CpFe(o-$C_6H_4Cl_2$)]PF_6,[24] and $Na_4P_2S_6\cdot 6H_2O$.[25]

$MnPS_3$ was prepared from the elements and $CdPS_3$ from CdS and red phosphorus by the literature method,[26] using decreased reaction times of two weeks for Mn and one week for Cd. ***Caution! Explosion hazard. Avoid rapid heating of these sealed-tube reactions.*** The intercalates $K_{0.4}Mn_{0.8}PS_3\cdot H_2O$, $Me_4N_{0.3}Mn_{0.85}PS_3\cdot H_2O$, and $Na_{0.8}Cd_{0.6}PS_3\cdot 1.5H_2O$ were prepared by the literature methods.[27] The sodium intercalate $Na_{0.6}Mn_{0.7}PS_3\cdot H_2O$ was prepared by Clement's modification[28] of the published method, by the reaction between NaCl and $K_{0.4}Mn_{0.8}PS_3\cdot H_2O$ in water. These compounds were characterized by XRD and elemental analyses before use.

$NaBPh_4$ was dried by heating to 100 °C for 4 h under vacuum and stored under nitrogen. The NMR solvents acetone-d_6 and acetonitrile-d_3 were dried over molecular sieves. Water was deionized. All other reagents and solvents were used as received from commercial suppliers.

All solution NMR spectra were obtained on a Bruker 300-MHz AM-300 instrument. ^1H and ^{13}C NMR spectra are referenced to internal solvent peaks; chemical shifts are in ppm relative to tetramethylsilane (TMS). ^{23}Na NMR spectra are referenced to an external standard sample of 3 M NaCl in D_2O. Wavelengths of ^{23}Na spectral lines were obtained by fitting the line shapes to a Lorentzian function.

Solid-state NMR spectra were obtained at fields of 4.7 and 9.4 T using Bruker MSL-200 and MSL-400 spectrometers, respectively. Resonance frequencies were as follows: MSL-200, ^1H, 200.13 MHz, ^{23}Na, 52.92 MHz, ^{13}C, 50.32 MHz; MSL-400, ^1H, 400.13 MHz, ^{23}Na, 105.84 MHz, ^{13}C, 100.61 MHz. Magic angle spinning in the range 2–5 KHz was performed using 7-mm external diameter zirconia rotors. ^{23}Na shifts were referenced to solid NaCl at 0 ppm. ^{13}C shifts were referenced to TMS at 0 ppm using adamantane as a secondary reference. ^{13}C spectra were acquired using cross polarization, which was set using adamantane.

Elemental analyses were carried out by the microanalytical service of this laboratory. The metal content of the samples was analyzed using atomic absorption (AA) spectroscopy. Since visual inspection suggested that the samples dissolved in concentrated HNO_3, no blanks were analyzed. As pointed out by a referee, others have experienced difficulty in obtaining good analytical results on similar compounds with AA. We have also observed this problem, which is reflected in the relatively large error bars on the metal stoichiometries (Table I). The stoichiometry of known starting materials was used to assign metal stoichiometries in most cases. For example, the formation of **4** from the known $K_{0.4}Mn_{0.8}PS_3\cdot H_2O$, as observed by XRD, requires that **4** contains at most 0.8 Mn.

Infrared spectra were recorded on KBr disks with a Perkin-Elmer 1710 FT-IR spectrometer. Powder X-ray diffraction spectra were recorded on a Philips PW 1729 powder diffractometer, controlled by a MAP 80 microcomputer, using Cu Kα radiation. XRD data are reported in the following form: *d* spacing; *hkl* lines observed.

[CpRu(benzo-15-crown-5)]PF_6 (1). An orange mixture of [CpRu(NCMe)$_3$]PF_6 (1200 mg, 2.76 mmol), benzo-15-crown-5 (1200 mg, 4.47 mmol) and 1,2-dichloroethane (50 mL) in an ampule was deoxygenated by bubbling nitrogen for 20 min. The ampule was sealed and then heated in an oil bath to 80 °C for 16 h, which caused a lightening of the orange color. The mixture was allowed to cool, and the solvent was removed on a rotary evaporator. The residual orange oil was stirred with toluene (100 mL) for 2 h to give a brown solid. The toluene solution was decanted, and the solid was washed with ether. The resulting brown powder was extracted into dichloromethane from which it was precipitated by addition of diethyl ether. Finally, the solid was recrystallized from acetone/diethyl ether at –20 °C to give 1086 mg (68% yield) of off-white needles. Anal. Calcd for $C_{19}H_{25}O_5RuPF_6$: C, 39.38; H, 4.36. Found: C, 39.20; H, 4.31. IR (KBr): 3105, 2921, 2869, 1527, 1514, 1486 (s), 1451, 1419, 1362, 1278 (s), 1206, 1132 (s), 1107 (s), 1082, 1031, 940, 908, 839 (vs), 770, 679, 610, 559 (s), 468, 425 cm^{-1}. ^1H NMR (acetone-d_6): δ 6.41–6.37 (m, 2H, Ar), 6.00–5.97 (m, 2H, Ar), 5.52 (5H, Cp), 4.41–4.36 (m, 2H, OCH_2), 4.23–4.16 (m, 2H, OCH_2), 3.85–3.82 (m, 4H, OCH_2), 3.71–3.65 (m, 8H, OCH_2). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 126.9 (C_6H_5–O), 81.6 (Ar), 80.7 (Cp), 74.1 (Ar), 72.2, 71.4, 70.6, 69.5 (4OCH_2).

[CpRu(benzo-15-crown-5)]Cl (2). [CpRu(benzo-15-crown-5)]PF_6 (240 mg, 0.41 mmol) was loaded and eluted with water down a column of Dowex 1×8-50 ion-exchange resin (30 cm × 0.5 cm), which had been saturated previously with NaCl solution and washed with water until no Cl^- was eluted. The solvent was removed from the pale yellow eluent in vacuo, and the resulting orange oil was recrystallized at –20 °C from acetone/diethyl ether to give 100 mg of white crystals (52% yield). Anal. Calcd for $C_{19}H_{25}O_5RuCl\cdot 2H_2O$: C, 45.10; H, 5.79; Cl, 7.01. Found: C, 45.56; H, 5.57; Cl, 8.7. IR (KBr): 3452, 3409, 3058, 3024, 2993, 2968, 2945, 2910, 2873, 1630, 1531, 1514, 1489, 1455, 1421, 1413, 1380, 1361, 1346, 1309, 1293, 1250, 1234, 1217, 1150, 1128, 1108, 1076, 1047, 1026, 937, 912, 869, 853, 830, 798, 770, 672, 611, 598, 529, 467, 429 cm^{-1}. ^1H NMR (D_2O): δ 6.12–6.10 (m, 2H, Ar), 5.64–5.62 (m, 2H, Ar), 5.18 (5H, Cp), 4.13–4.09 (m, 2H, OCH_2), 3.85–3.78 (m, 2H, OCH_2), 3.69–3.68 (m, 4H, OCH_2), 3.51–3.49 (m, 8H, OCH_2). $^{13}C\{^1H\}$ NMR (D_2O): δ 123.6 (C_6H_5–O), 78.8 (Ar), 78.1 (Ar), 71.1 (Cp), 68.8, 68.3, 67.6, 66.6 (4 OCH_2).

{CpRu[o-$C_6H_4(OMe)_2$]}PF_6 (3). **3** was prepared by the same method used for **1** as a white powder in 30% yield after purification by chromatography on alumina with acetone and recrystallization from acetone/diethyl ether at –20 °C. Anal. Calcd for $C_{13}H_{15}O_2RuPF_6$: C, 34.75; H, 3.37. Found: C, 34.45; H, 3.30. IR (KBr): 3123, 3043, 2955, 1533, 1524, 1489 (s), 1465, 1443 (s), 1419, 1277 (s), 1226, 1183, 1154, 1106, 1012 (s), 975, 835 (vs), 752, 672, 582, 559 (s), 533, 500, 424 cm^{-1}. ^1H NMR (acetone-d_6): δ 6.53–6.51 (m, 2H, Ar), 6.00–5.98 (m, 2H, Ar), 5.94 (5H, Cp), 2.96 (6H, Me). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 127.2 (quat Ar), 81.0, 80.3 (2 Ar), 72.8 (Cp), 58.4 (Me).

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(15-crown-5)$_{0.33}$K$_{0.4}$Mn$_{0.8}$PS$_3$ (4). A mixture of $MnPS_3$ (75 mg, 0.41 mmol), 15-crown-5 (500 mg, 2.27 mmol), and KCl (375 mg, 5.0 mmol) was soaked in 10 mL of H_2O for 3 d. Filtration gave a green powder, which was washed with water and acetone. XRD showed this to be a mixture of $MnPS_3$, product **4**, and the known compound $K_{0.4}Mn_{0.8}PS_3 \cdot H_2O$. Repetition of the reaction with similar amounts of crown ether and KCl after two more cycles gave pure **4**. XRD: d = 15.5 Å; 00l with l = 1–5 and 8–11. IR (KBr): 2924, 2855, 1626, 1460, 1355, 1117, 937, 858, 614, 590, 555 (s), 449 cm^{-1}.

(15-crown-5)$_{0.43}$K$_{0.5}$Cd$_{0.75}$PS$_3$·H$_2$O (5). A mixture of $CdPS_3$ (630 mg, 2.62 mmol), 15-crown-5 (3.2 g, 14.5 mmol), KCl (2.4 g, 32 mmol), $KHCO_3$ (2.4 g, 24 mmol), K_2CO_3 (3.33 g, 24 mmol) and EDTA (700 mg, 2.4 mmol) was soaked in 50 mL of H_2O for 5 d. Filtration gave a white powder, which was washed with water and acetone. XRD showed this to be a mixture of product **5** and the known compound $K_{0.5}Cd_{0.75}PS_3 \cdot H_2O$. Further reaction with portions of KCl (about 2 g) and 15-crown-5 (about 1 g) in water gave, after three more cycles, pure **5**. XRD: d = 15.6 Å; 00l with l = 1–5 and 8–10. IR (KBr): 2946, 2892, 2858, 1620, 1438, 1355, 1303, 1241, 1118 (s), 1028, 938, 858, 826, 604 (s), 585 (s), 551 (vs), 450 cm^{-1}.

(15-crown-5)$_{0.43}$K$_{0.3}$Na$_{0.2}$Cd$_{0.75}$PS$_3$·H$_2$O (7a–b) by Ion Exchange on 5. Compound **5** (375 mg, 1.08 mmol), NaCl (7.8 g, 133 mmol), and 15-crown-5 (3.13 g, 14.2 mmol) were stirred slowly in 60 mL of water for 3 d. The usual workup gave a white powder whose XRD spectrum was the same as that of the starting material. IR (KBr): 2943, 2893, 2857, 1618, 1438, 1353, 1302, 1241, 1118 (s), 1091 (s), 1028, 938, 858, 820, 603 (vs), 585 (vs), 551 (vs), 450 cm^{-1}. [In a separate experiment, a similar product of incomplete exchange, **7a**, was also characterized by elemental analysis: Anal. Calcd for (15-crown-5)$_{0.43}$K$_{0.3}$Na$_{0.2}$Cd$_{0.75}$PS$_3$·H$_2$O: C, 15.2; H, 3.14; Cd, 24.8; K, 3.44; Na, 1.35. Found: C, 15.1; H, 2.64; Cd, 26.2; K, 2.37; Na, 0.80.] Further exchanges (three cycles) gave a white powder, **7b**, indistinguishable from **7a** by XRD, IR, or analysis. Found: C, 15.3; H, 2.60; Cd, 25.1; K, 2.08; Na, 0.76.

General Ion-Exchange Intercalation Method. The host ($MnPS_3$ or $CdPS_3$ preintercalated with a small mobile cation) and the guest, typically in a ratio of 1:0.5, were put in an ampule with a stirrer bar in a 1:1 mixture of acetone and water. The mixture was frozen and evacuated. The ampule was sealed and heated in an oil bath with stirring at the indicated temperature (typically 60–80 °C) for the indicated times (usually 1–10 days). After workup, which consisted of filtration followed by washing the solid with acetone and water and drying in vacuo, the progress of reaction was monitored by XRD. If reaction was incomplete, the procedure was repeated with a fresh solution of the guest molecule (quantities as noted below).

ZnPS$_3$·3H$_2$O (Amorphous). A solution of $Na_4P_2S_6 \cdot 6H_2O$ (3.06 g, 6.74 mmol) in 125 mL of hot water was added, with stirring, to a solution of 20 g (69.6 mmol) of $ZnSO_4 \cdot 7H_2O$ in 150 mL of water. A white precipitate formed immediately, and upon complete addition the mixture was a white colloidal suspension. It was stirred for 15 min, and the white solid was collected on a frit, washed with hot water, and then dried in vacuo to yield 2.58 g (78%) of a free-flowing white powder. XRD: This material and all its derivatives described below are amorphous. IR (KBr): 3543 (br), 1607, 597–586 (br), 452 cm^{-1}. Anal. Calcd for $ZnPS_3 \cdot 3H_2O$: Zn, 26.51; H, 2.46. Found: Zn, 26.33; H, 1.70.

General Procedure for Intercalation in ZnPS$_3$ Materials. The Zn starting material and the guest molecule were stirred at room temperature in the solvent given below in the air for the indicated time, then worked up as for the Mn- and Cd-containing materials.

(15-crown-5)$_{0.3}$Na$_{0.5}$Zn$_{0.75}$PS$_3$·H$_2$O (6). $ZnPS_3 \cdot 3H_2O$ (230 mg, 1.04 mmol), NaCl (1.18 g, 20.2 mmol), 15-crown-5 (1225 mg, 5.56 mmol), and 25 mL of H_2O; 3 h; wash with acetone/water and methanol/water; white powder. IR (KBr): 3478, 2917, 2872, 1615, 1473, 1453, 1352, 1292, 1248, 944, 859, 803, 597 (s), 581 (s), 453 cm^{-1}. Solid-state ^{23}Na NMR δ −23 ppm (br).

[CpRu(benzo-15-crown-5)]$_{0.23}$Na$_{0.4}$Mn$_{0.7}$PS$_3$·H$_2$O (8). Compound **1** (300 mg, 0.52 mmol), $Na_{0.6}Mn_{0.7}PS_3 \cdot H_2O$ (300 mg, 1.5 mmol), and 8 mL of 1:1 water/acetone; 60 °C, 4 d; green powder. XRD: d = 15.2 Å; 00l with l = 1–10. IR (KBr): 3427, 3062, 2918, 2867, 1620, 1524, 1512, 1480, 1442, 1415, 1359, 1271, 1202, 1105, 1027, 937, 847, 801, 771, 680, 610 (vs), 593 (vs), 554 (vs), 450, 423 cm^{-1}.

[CpRu(benzo-15-crown-5)]$_{0.28}$(Me$_4$N)$_{0.02}$Mn$_{0.85}$PS$_3$·H$_2$O (9). $Me_4N_{0.3}Mn_{0.85}PS_3 \cdot H_2O$ (350 mg, 1.63 mmol), compound **1** (375 mg, 0.65 mmol), and 10 mL of 1:1 acetone/water; 80 °C; 4 d; then fresh **1** (100 mg, 0.17 mmol); 80 °C, 4 d; then a second portion of fresh **1** (100 mg, 0.17 mmol); 80 °C; 4 d; green-brown solid. XRD: d = 15.2 Å; 00l with l = 1–10. IR (KBr): 3432, 3067, 2863, 1614, 1514, 1441, 1415, 1357, 1270, 1205, 1106, 1084, 929, 842, 801, 772, 680, 611 (vs), 590 (vs), 554 (vs), 450, 423 cm^{-1}.

Reaction of a Crown-Containing Intercalate with Aqueous Na$^+$. Compound **9** (90 mg, 0.29 mmol) was stirred with $NaPF_6$ (10 mg, 0.06 mmol) in 20 mL of water overnight. Filtration, washing, and drying as before gave a brown-green solid whose powder pattern was identical with that of the starting material. Elemental analysis showed loss of N and uptake of Na; the procedure was repeated to cause further exchange. Anal. Found for **9**: N, 0.20; C, 20.81; H, 2.43; Mn, 14.57; Na, 0.05. Found after first treatment with Na$^+$: N, 0.12; C, 20.81; H, 2.22; Mn, 15.05; Na, 0.07. Found after second treatment: N, <0.1%; C, 20.78; Mn, 14.57; Na, 0.10. Similar results were obtained with NaCl, but in both cases the numbers are so small as to be within the limits of error of the analysis.

[CpRu(benzo-15-crown-5)]$_{0.27}$Na$_{0.5}$Cd$_{0.6}$PS$_3$·H$_2$O (10). Compound **1** (300 mg, 0.52 mmol), $Na_{0.8}Cd_{0.6}PS_3 \cdot 1.5\,H_2O$ (300 mg, 1.08 mmol), and 14 mL of 1:1 acetone/water; 60 °C; 3 d; then fresh **1** (100 mg, 0.17 mmol); 60 °C; 1 d; beige solid. XRD: d = 15.2 Å; 00l with l = 1–4 and 7–10. IR (KBr): 3442, 3058, 2867, 1619, 1523, 1480, 1441, 1414, 1358, 1269, 1201, 1104, 1024, 936, 847, 770, 596 (s), 552 (vs), 451, 423 cm^{-1}. Solid-state ^{13}C MAS-NMR: δ 127 (br), 81 (br), 70 (v br).

[CpRu(benzo-15-crown-5)]$_{0.34}$Na$_{0.1}$Zn$_{0.8}$PS$_3$·H$_2$O (11). Compound **1** (139 mg, 0.24 mmol), Na intercalate **17** (90 mg, 0.41 mmol), and 20 mL of 1:1 acetone/water; 1 d; beige solid. IR (KBr): 3519, 3436, 3073, 2917, 2871, 2012, 1615, 1524, 1480, 1446, 1414, 1358, 1273, 1200, 1104, 1026, 937, 849, 802, 763, 596 (s), 579 (s), 454, 424 cm^{-1}. Solid-state ^{23}Na NMR: δ −13.5 ppm (br).

[CpFe(C$_6$Me$_6$)]$_{0.28}$Na$_{0.5}$Cd$_{0.6}$PS$_3$·H$_2$O (12). [CpFe(C$_6$Me$_6$)]PF$_6$ (300 mg, 0.70 mmol), $Na_{0.8}Cd_{0.6}PS_3 \cdot 1.5H_2O$ (200 mg, 0.72 mmol), and 14 mL of 1:1 acetone/water; 60 °C, 2 d; then more [CpFe(C$_6$Me$_6$)]PF$_6$ (480 mg, 1.12 mmol); 60 °C; 3 d; brown powder. XRD: d = 13.5 Å; 00l with l = 1–3, 5, and 8. IR (KBr): 3433, 2961, 1625, 1388, 1071, 1020, 871, 843, 827, 601 (s), 586 (s), 552 (vs), 505, 450 cm^{-1}.

[CpRu(p-cymene)]$_{0.21}$Na$_{0.4}$Mn$_{0.7}$PS$_3$·H$_2$O (13). [CpRu(p-cymene)]PF$_6$ (300 mg, 0.67 mmol), $Na_{0.6}Mn_{0.7}PS_3 \cdot H_2O$ (150 mg, 0.75 mmol), and 4 mL of 1:1 acetone/water; 50 °C; 1 d; green powder. XRD: d = 12.2 Å; 00l with l = 1–8. IR (KBr): 3424, 3057, 2963, 1619, 1476, 1413, 1384, 1261, 1090, 1056, 877, 847, 803, 593 (vs), 554 (vs), 450 cm^{-1}.

[CpRu(p-cymene)]$_{0.25}$(Me$_4$N)$_{0.05}$Mn$_{0.85}$PS$_3$·H$_2$O (14). [CpRu(p-cymene)]PF$_6$ (600 mg, 1.35 mmol), $Me_4N_{0.3}Mn_{0.85}PS_3 \cdot H_2O$ (535 mg, 2.5 mmol), and 10 mL of 1:1 acetone/water; 80 °C; 5 d; green powder. XRD: d = 12.3 Å; 00l with l = 1–4 and 7–8; and 200, 040. IR (KBr): 3433, 2963, 1619, 1413, 1384, 1093, 1021, 874, 612 (s), 590 (s), 555 (vs), 450 cm^{-1}.

[CpFe(o-C$_6$H$_4$Cl$_2$)]$_{0.4}$K$_{0.02}$Mn$_{0.8}$PS$_3$·H$_2$O (15). $K_{0.4}Mn_{0.8}PS_3 \cdot H_2O$ (110 mg, 0.54 mmol), [CpFe(o-C$_6$H$_4$Cl$_2$)]PF$_6$ (300 mg, 0.73 mmol), and 10 mL of 1:1 acetone/water; 70 °C; 2 d; red-brown solid. XRD: d = 12.6 Å; 00l with l = 1–5; and h00 with h = 2–3. IR (KBr): 3416, 3051, 2962, 1619, 1416, 859, 746, 663, 607 (s), 555 (s), 492, 448 cm^{-1}.

[Cp*Ru(C$_6$H$_6$)]$_{0.26}$K$_{0.1}$Mn$_{0.8}$PS$_3$·H$_2$O (16). [Cp*Ru(C$_6$H$_6$)]PF$_6$ (150 mg, 0.33 mmol), $K_{0.4}Mn_{0.8}PS_3 \cdot H_2O$ (50 mg, 0.25 mmol), and 4 mL of 1:1 acetone/water; 60 °C, 2 d; green powder. XRD: d = 13.6 Å; 00l with l = 1, 2, 4–5, and 8. IR (KBr): 3425, 2964, 2908, 1620, 1472, 1440, 1381, 1077, 1029, 979, 793, 612 (s), 591 (s), 556 (vs), 450 cm^{-1}.

Na$_{0.4}$Zn$_{0.8}$PS$_3$·1.75H$_2$O (17). NaCl (2.5 g, 42.7 mmol), $ZnPS_3 \cdot 3H_2O$ (500 mg, 2.03 mmol), and 25 mL of H_2O; 2.5 h; white powder. IR (KBr): 3543 (br), 1607, 1087 (br), 1025 (br), 597–586 (br), 452 cm^{-1}. Solid-state ^{23}Na NMR: δ −10 ppm (br).

(Me$_4$N)$_{0.5}$Zn$_{0.75}$PS$_3$·H$_2$O (18). Me_4NI (4.5 g, 22.4 mmol), $ZnPS_3 \cdot 3H_2O$ (500 mg, 2.03 mmol), and 100 mL of H_2O; 1 d; white powder. IR (KBr): 3434, 1611, 1480, 947, 597, 454 cm^{-1}.

[CpFe(C$_6$Me$_6$)]$_{0.42}$Zn$_{0.8}$PS$_3$·2H$_2$O (19). $ZnPS_3 \cdot 3H_2O$ (120 mg, 0.48 mmol), [CpFe(C$_6$Me$_6$)]PF$_6$ (690 mg, 1.61 mmol), 10 mL of water; and 50 mL of acetone; 1 d; orange solid. IR (KBr): 3416 (br), 3089, 2932, 1617, 1447, 1416, 1388, 1070, 1006, 853, 803, 595 (vs), 580 (vs), 505, 454 cm^{-1}.

[CpFe(C$_6$Me$_6$)]$_{0.39}$Na$_{0.05}$Zn$_{0.8}$PS$_3$·1.5H$_2$O (20). Na intercalate **17** (120 mg, 0.55 mmol), [CpFe(C$_6$Me$_6$)]PF$_6$ (150 mg, 0.35 mmol), and 30 mL of 2:1 acetone/water; 1 d; orange powder. IR (KBr): 3418, 3086, 2961, 1614, 1446, 1416, 1387, 1071, 1019, 853, 594 (s), 579 (s), 505, 454 cm^{-1}. Solid-state ^{23}Na NMR: δ −6.5 ppm (br).

Na$^+$ Binding by 1 in CD$_3$CN. (a) ^{23}Na NMR. $NaBPh_4$ (10 mg, 2.92 $\times$ 10^{-2} mmol) was dissolved in 2.0 mL of CD_3CN, and a ^{23}Na NMR spectrum was obtained. Aliquots (200 μL) of a stock solution of **1** (36 mg, 6.21 $\times$ 10^{-2} mmol, in 2 mL of CD_3CN) were added to the tube, and the spectral changes were monitored. The resulting titration curves are given in Figure 4.

(b) $^{13}C\{^1H\}$ NMR. An NMR tube was charged with a solution of **1** (78 mg, 0.135 mmol) in 2.5 mL of CD_3CN. The $^{13}C\{^1H\}$ NMR spectrum of the sample was monitored as a series of eight 0.3-mL aliquots of a 0.111 M solution of $NaBPh_4$ in CD_3CN was added to the solution. The signals due to the crown ether methylene carbons underwent chemical shift changes of about 1 ppm; these are plotted in Figure 3. A control experiment with the model compound $\{CpRu[o\text{-}C_6H_4(OMe)_2]\}PF_6$ (**3**) showed no such changes, as also observed for a titration of **2** with NaCl in D_2O.

The solvent was removed from the NMR solution and repeated recrystallization of the residue from acetone/ether at −20 °C gave white crystals of $[CpRu(benzo\text{-}15\text{-}crown\text{-}5)(NaPF_6)]BPh_4$ (**21**) suitable for a single-crystal X-ray study. Anal. Calcd for $C_{43}H_{45}BO_5RuNaPF_6$: C, 56.03; H, 4.93; Na, 2.50. Found: C, 55.79; H, 4.70; Na 2.87. IR (KBr): 3055, 1527, 1481, 1450, 1419, 1270, 1200, 1120, 1106, 1026, 948, 906, 854 (s), 843, 781, 770, 745, 733, 721, 710, 672, 626, 607, 561, 519, 427 cm^{-1}.

X-ray Crystal Structure Determination of 21. A crystal was sealed in a Lindemann glass capillary and transferred to the goniometer head of an Enraf-Nonius CAD4 diffractometer interfaced to a PDP 8 mini-computer. Unit cell parameters were calculated from the setting angles of 25 carefully-centered reflections. Three reflections were chosen as intensity standards and were measured every 3600 s of X-ray exposure time, and three orientation controls were measured every 250 reflections.

The data were corrected for Lorentz and polarization effects, and an empirical absorption correction[29] based on azimuthal scan data was applied. Equivalent reflections were merged and systematically absent reflections rejected. The ruthenium atom position was determined from a Patterson synthesis. Subsequent difference Fourier syntheses revealed the positions of other non-hydrogen atoms. Non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares procedures. Hydrogen atoms were placed in estimated positions (C–H = 0.96 Å) with fixed isotropic thermal parameters and refined riding their supporting carbon atoms.

A Chebyshev weighting scheme[30] was applied and the data were corrected for the effects of anomalous dispersion and isotropic extinction (via an overall isotropic extinction parameter[31]) in the final stages of refinement. All crystallographic calculations were performed using the CRYSTALS suite[32] on a MicroVAX 3800 computer in the Chemical Crystallography Laboratory, Oxford, England. Neutral atom scattering factors were taken from the usual sources.[33]

$[CpRu(benzo\text{-}15\text{-}crown\text{-}5)(NaPF_6)]PF_6$ (22). Compound **1** (135 mg, 0.233 mmol) and $NaPF_6$ (40 mg, 0.238 mmol) were dissolved in 50 mL of CH_3CN and stirred for 2 h. The solution was filtered and the solvent removed on a rotary evaporator. The orange oil was recrystallized twice from acetone/ether at −20 °C to give 60 mg of off-white microcrystals (34% yield). Anal. Calcd for $C_{19}H_{25}O_5RuNaP_2F_{12}$: C, 30.53; H, 3.38; Na, 3.08. Found: C, 30.51; H, 3.35; Na 3.30. IR (KBr): 3062, 2963, 2922, 1529, 1509, 1485, 1449, 1417, 1365, 1293, 1262, 1200, 1127, 1106, 1025, 942, 840 (vs), 560 (s), 421 cm^{-1}. Solid-state ^{23}Na NMR: δ −26 ppm (br).

Acknowledgment. D.S.G. thanks NATO for a postdoctoral fellowship administered by the National Science Foundation. We thank the SERC for a quota award to A.R.B. and a grant toward the NMR equipment and Drs. P. D. Beer, R. Clement, C. M. Dobson, S. J. Heyes, D. O'Hare, and G. C. Saunders for helpful discussions.

Supplementary Material Available: Crystallographic data for **21**, including an ORTEP diagram and tables giving crystal data, details of the structure determination, bond lengths and angles, fractional atomic coordinates, and thermal parameters (14 pages). Ordering information is given on any current masthead page.

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