$Cs_3[Ir_9(CO)_{20}]$ was filtered off, washed with a 10% solution of CsCl (3 × 5 mL), and vacuum-dried. The cesium salt was dissolved in methanol, and the brown solution was cautiously layered with a 0.5% solution of benzyltrimethylammonium chloride in 2-propanol; the slow diffusion of the two solvents produced prismatic dark brown crystals of $[NMe_3-(CH_2Ph)]_3[Ir_9(CO)_{20}]$. The yields are rather low and variable (5–8% based on starting $Ir_4(CO)_{12}$), depending on the experimental conditions. Salts of other bulky cations can be obtained in a similar way.

X-ray Analysis. Intensity Data Collection, Structure Solution, and Refinement. Crystal data and other experimental details are summarized in Table III. Intensity data were collected on an Enraf-Nonius CAD-4 automated diffractometer using Mo Kα radiation (λ = 0.710 73 Å) with a graphite crystal monochromator in the incident beam. Standard CAD-4 setting, indexing, and data collection programs were used. Periodic measurements of three standard reflections revealed a crystal decay, on X-ray exposure, which was evaluated as about 17% on F_o at the end of data collection. Intensities were corrected for Lorentz, polarization, and decay effects. An empirical absorption correction was applied to the intensities, based on ψ scans (ψ = 0–360°) of suitable reflections with χ values close to 90° as described in ref 23. The structure was solved by direct methods (MULTAN) and difference Fourier syntheses and refined by full-matrix least-squares methods, the minimized function being $\sum w(F_o - k|F_c|)^2$. Individual weights were given as $w = 1/\sigma^2(F_o)$ where $\sigma(F_o) = \sigma(F_o^2)/2F_o$, $\sigma(F_o^2) = [\sigma^2(I) + (pI)^2]^{1/2}/Lp$, and p, the "ignorance factor", was equal to 0.03. Scattering factors and anomalous dispersion corrections were taken from ref 24.

The final difference Fourier map showed peaks not exceeding 1.2 e/Å^3 near the metal atoms.

Fractional atomic coordinates of non-hydrogen atoms are listed in Table IV. All computations were done on a PDP 11/73 computer using the Enraf-Nonius structure determination package (SDP) and the physical constants tabulated therein,[25] MULTAN[26] for direct methods, and ORTEP for drawings.[27]

Supplementary Material Available: Listings of thermal parameters (Table 1S), complete distances and angles (Table 2S), calculated cation hydrogen atom positions (Table 3S), isotropic thermal parameters for cation non-hydrogen atoms (Table 4S), and crystal data (Table 5S) (11 pages); a listing of observed and calculated structure factors (Table 6S) (47 pages). Ordering information is given on any current masthead page.

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X-ray Powder Diffraction Studies of Alkalides and Electrides That Contain 15-Crown-5

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Introduction

Crystalline alkalides and electrides were first synthesized in 1974 and 1983, respectively.[1,2] Alkalides contain alkali metals in both the cationic and anionic forms, while in electrides, charge compensation is made, not by conventional anions but by trapped electrons. Single-crystal X-ray structures have been determined and published for 10 alkalides and 2 electrides,[3–9] and the

structures of an additional 14 alkalides and 2 electrides have been determined.[10]

Due to the thermal instability and reactivity of these compounds, it is often difficult to grow single crystals. Some show evidence of phase transitions. X-ray powder diffraction studies of alkalides and electrides can provide information about structures, thermal stabilities, and thermally induced phase transitions. In addition, the homogeneity of a polycrystalline sample can be assessed.

We chose for this study the alkalides and electrides formed with the crown ether 15-crown-5 (15C5, 1,4,7,10,13-pentaoxacyclopentadecane) because of the wide variety of compounds that can be made. Because they are reasonably stable, easy to prepare, relatively inexpensive, and soluble in aprotic solvents such as dimethyl ether, such compounds are promising candidates for use as reductants.

Compounds of this type were first synthesized in 1985,[11] and five single-crystal structures have been determined by X-ray diffraction. The alkalides $Rb^+(15C5)_2Na^-$, $Rb^+(15C5)_2Rb^-$, and $Cs^+(15C5)_2K^-$ are monoclinic ($C2/m$),[8,10] while $Cs^+(15C5)_2Na^-$ and $Cs^+(15C5)_2e^-$ belong to the triclinic system ($P\bar{1}$).[10] Others have been prepared as polycrystalline samples, but so far it has not been possible to grow single crystals. X-ray powder diffraction provides a way to determine the crystallographic system and cell parameters and to see whether complications such as phase transitions interfere with crystal growth.

Experimental Section

The compounds $M_a^+(15C5)_2M_b^-$ and $M^+(15C5)_2e^-$ were synthesized in a vacuum-tight apparatus called a K-cell by using previously reported techniques.[6,12,13] In all the experimental steps, low temperatures and inert atmosphere conditions must be used due to the air and thermal sensitivities of these compounds.

A Rigaku D/max-RBX rotating-anode diffractometer equipped with a scintillation counter detector and a graphite monochromator to yield Cu Kα (wavelength 1.541 84 Å) radiation was used under the control of a DEC Microvax computer. All data were recorded by scans at 45 kV and 80 mA. The low-temperature attachment permitted evacuation to about 35 mTorr and the temperature could be varied from 80 to 300 K.

Results and Discussion

The X-ray powder diffraction patterns were recorded at several temperatures for the nine compounds synthesized so far with the crown ether 15C5. Two copper peaks at 2θ = 43.28 and 50.41° (wavelength 1.541 84 Å) from the sample holder provided calibration points. All attempts to obtain a well-defined powder pattern for $K^+(15C5)_2e^-$ were unsuccessful, as even the best diffractogram was poorly resolved.

The temperature dependence of the diffractograms showed two kinds of behavior: (1) For the compounds $Rb^+(15C5)_2Na^-$, $Cs^+(15C5)_2Na^-$, $Rb^+(15C5)_2Rb^-$, $Cs^+(15C5)_2K^-$, $Cs^+(15C5)_2e^-$, and $Rb^+(15C5)_2e^-$, the pattern difference from 80 to 200 K consisted of a shift to lower angles of nearly all the peaks. Above 200 K the peak positions did not shift appreciably but there was an increasing amorphous background relative to the significantly lower peak intensities. (2) For the compounds $K^+(15C5)_2Na^-$ and $K^+(15C5)_2K^-$, some peaks disappeared and new ones appeared

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Table I. Crystallographic Data from Single-Crystal and Powder X-ray Diffraction Studies

	vol, Å³	*a*, Å	*b*, Å	*c*, Å	*β*, deg	*T*, K	
Rb⁺(15C5)₂Na⁻	1562.4 (7)ᵃ	11.555 (3)	13.587 (3)	9.958 (2)	92.03 (2)	210	crystalᵇ
monoclinic *C2/m*	1564.7 (9)	11.570 (4)	13.642 (4)	9.917 (3)	91.67 (3)	200	powderᶜ
	1542.8 (7)	11.376 (3)	13.687 (4)ᵈ	9.914 (3)	91.99 (2)	80	powder
Rb⁺(15C5)₂Rb⁻	1701.2 (8)	11.635 (3)	13.855 (5)	10.556 (3)	91.18 (2)	220	crystal
monoclinic *C2/m*	1706.8 (12)	11.674 (5)	13.881 (6)	10.553 (4)	90.88 (5)	200	powder
	1661.8 (7)	11.598 (3)	13.696 (3)	10.463 (2)	91.10 (2)	80	powder
Cs⁺(15C5)₂K⁻	1676.6 (8)	11.537 (4)	13.679 (3)	10.624 (3)	90.12 (2)	210	crystal
monoclinic *C2/m*	1658.5 (7)	11.540 (3)	13.511 (3)	10.637 (3)	90.14 (2)	80	powder
K⁺(15C5)₂Na⁻	1529.9 (5)	11.573 (2)	13.623 (3)	9.705 (2)	90.98 (1)	80	powder
monoclinic *C2/m*							
K⁺(15C5)₂K⁻	1682.9 (8)	12.089 (3)	13.799 (4)	10.087 (4)	91.05 (2)	200	powder
monoclinic *C2/m*							
Cs⁺(15C5)₂e⁻	733.1 (11)	8.597 (4)	8.886 (8)	9.941 (9)	α = 102.91 (8)	215	crystal
triclinic *P1̄*					β = 90.06 (6)		
					γ = 97.74 (6)		
Cs⁺(15C5)₂Na⁻	792.1 (17)	8.661 (11)	9.010 (9)	10.315 (15)	α = 93.24 (10)	210	crystal
triclinic *P1̄*					β = 92.21 (11)		
					γ = 99.34 (10)		

ᵃ Estimated standard deviation of the last digit is given in parentheses. ᵇ Crystal means single-crystal X-ray studies.[6,10,17] ᶜ Powder means powder X-ray data from this work. All the peaks up to 2θ = 40° (wavelength 1.541 84 Å) were used in the refinement. ᵈ Note elongation of the *b* axis upon cooling in spite of contraction of the cell volume. The reason is unknown.
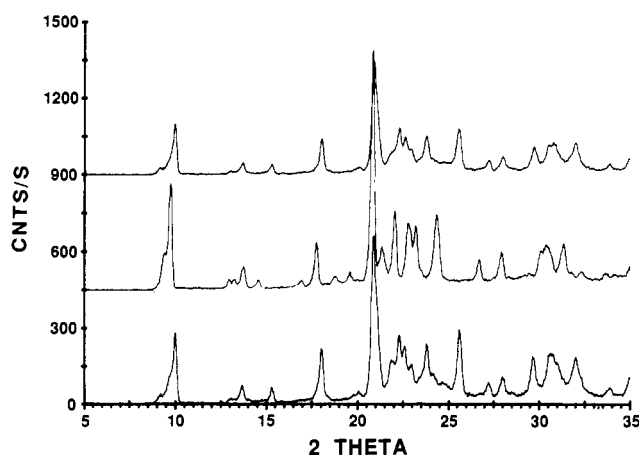

Figure 1. Smoothed X-ray diffraction powder patterns for K⁺-(15C5)₂Na⁻: bottom, 80 K; middle, 200 K; top, 80 K (afterward). Note the presence of a reversible phase transition between these temperatures (wavelength 1.541 84 Å).

between 80 and 200 K, indicating that a structural change had occurred within this temperature range.

For each compound, after the temperature had been raised to 200 K, the sample was again cooled to 80 K. For all samples except Cs⁺(15C5)₂e⁻, the initial X-ray pattern (line positions) was recovered. The diffractograms of K⁺(15C5)₂Na⁻ shown in Figure 1 illustrate this recovery. Although the recovery was nearly quantitative for Rb⁺(15C5)₂Na⁻, Rb₊(15C5)₂Rb⁻, Rb⁺(15C5)₂e⁻, K⁺(15C5)₂Na⁻, and Cs⁺(15C5)₂Na⁻, this was not the case for K⁺(15C5)₂K⁻ and Cs⁺(15C5)₂K⁻. For these compounds, the peak positions were restored, but the peaks were significantly broader and the resolution was poorer.

The structures of five compounds in this series had been previously determined by single-crystal X-ray diffraction. Their space groups and cell parameters are given in Table I. The single-crystal data were used to index the powder diffraction peaks. A computer program[14] was used to calculate the peak positions and intensities from the single-crystal data. All atoms except hydrogen were included.

A second computer program[15] used these data to yield a simulated diffractogram for comparison with the experimental data. However, the calculated peak intensities, especially for the low-angle peaks, do not match the experimental intensities. The variability of peak intensities results from the need to pack the powder into a depression on the copper holder in order to make
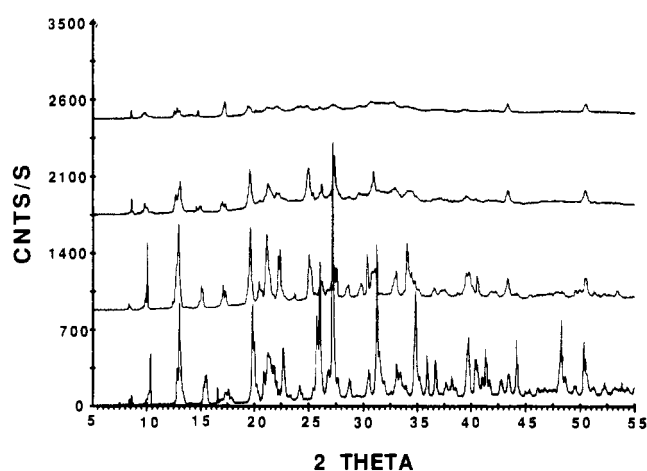

Figure 2. Smoothed X-ray diffraction powder patterns for Rb⁺-(15C5)₂Rb⁻. From bottom to top: 80, 200, 230, 250 K (wavelength 1.541 84 Å). When the sample temperature is returned to 80 K, the initial pattern is recovered except that the intensities are not completely reproduced.

it stick. This creates preferential orientation and drastically affects the peak intensities. This common problem in powder X-ray studies is difficult to overcome with these reactive and unstable compounds and makes data of the type obtained here unsuitable for complete structure determination. The effect is particularly noticeable for the low-angle peaks. It even yields apparent structure on these peaks when there should be none. This presumably occurs as the beam scans different crystallites when passing through a given reflection.

The temperature study shows that the relative intensity of the amorphous background increases with temperature but it is always present, even at 80 K. The intensity of the diffraction peaks decreases as the temperature increases. At 250 K the X-ray pattern is still discernible for K⁺(15C5)₂Na⁻ and Rb⁺(15C5)₂Na⁻. For the other compounds the diffraction peaks are weak or absent. Almost all the diffraction peaks disappear at room temperature, even for the most stable compounds. The dramatic effects of increasing temperature are illustrated in Figure 2, which shows the diffractograms of Rb⁺(15C5)₂Rb⁻ at various temperatures. As the temperature is increased from 80 to 200 to 230 K, the marked intensity decrease and peak broadening (reversible phenomena) probably correspond to thermal motions of the atoms in the crown ring. Disorder in sandwich crown ether compounds is frequently encountered.[16] For Cs⁺(15C5)₂e⁻, the irreversible

(14) Computer program designed by R. Marsolais, Rutgers University, 1985.
(15) Simulation program, Rigaku Co.

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loss of crystallinity that occurs at 200 K (a temperature at which the compound is stable) may correspond to mechanical destruction of the crystals, leading to a severe mosaic spread and tending toward amorphous character.

Single-crystal data at or near 200 K for $Rb^+(15C5)_2Na^-$, $Rb^+(15C5)_2Rb^-$, and $Cs^+(15C5)_2K^-$ (monoclinic, $C2/m$) were used to simulate the X-ray powder patterns. A good match of the peak positions allowed us to index the diffraction peaks and showed that the powder samples were monophasic. This is important, since single crystals for structure determination can often be picked from a mixture that contains other compounds or structural types.

The refinement of the X-ray powder pattern for these three known compounds at 200 K gives the data in Table I. For $Rb^+(15C5)_2Na^-$ and $Rb^+(15C5)_2Rb^-$, the data at 80 K are also included. Only a small change in the cell parameters occurs as the temperature is decreased from 200 to 80 K.

The two compounds of unknown structure, $K^+(15C5)_2K^-$ and $K^+(15C5)_2Na^-$, had powder patterns sufficiently similar to those of known structure to permit refinement, although complications resulted from the phase transition observed for these two compounds.

The XRD powder pattern of $K^+(15C5)_2Na^-$ at 80 K is very similar to that of $Rb^+(15C5)_2Na^-$, so that refinement of the cell parameters of the former compound could be readily made by starting with structural data for the latter compound. However, the phase transition that occurred between 80 and 200 K yielded a new pattern that did not permit refinement and may have resulted from a mixture. Therefore, Table I contains cell parameters for $K^+(15C5)_2Na^-$ only at 80 K.

Interestingly, the powder pattern of $K^+(15C5)_2K^-$ at 200 K is similar to that of $Rb^+(15C5)_2Na^-$ at 80 K, permitting refinement at 200 K. The pattern at 80 K for the former compound is sufficiently different that refinement was not possible.

Both $Cs^+(15C5)_2Na^-$ and $Cs^+(15C5)_2e^-$ are triclinic ($P\bar{1}$).[10,17] In each case, one of the $-CH_2-$ groups is disordered and the single-crystal data were refined by using half-occupancy for each site. The program used for the simulation of powder patterns does not allow inclusion of partial occupancy. Nevertheless, the simulated powder patterns obtained by ignoring the disorder agreed well with the observed patterns. Because of missing low-angle diffraction peaks, however, it was not possible to refine the powder diffraction data.

The XRD powder patterns of $Rb^+(15C5)_2e^-$ and $K^+(15C5)_2e^-$ were also obtained. However, severe broadening of the diffraction peaks of the latter and the very low intensity at low angles of the former made the study difficult. Also, it is difficult in the synthesis of $Rb^+(15C5)_2e^-$ and $K^+(15C5)_2e^-$ to avoid formation of mixtures with the corresponding alkalide. It appears from the diffraction data that $Rb^+(15C5)_2e^-$ belongs to the monoclinic system. The data for $K^+(15C5)_2e^-$ were not good enough to permit assignment of the crystal system.

Summary

From these results several points can be made: (1) The two sodides $K^+(15C5)_2Na^-$ and $Rb^+(15C5)_2Na^-$, the two potassides $Cs^+(15C5)_2K^-$ and $K^+(15C5)_2K^-$, and the rubidide Rb^+-$(15C5)_2Rb^-$ all belong to the monoclinic system and are probably isostructural. (2) For $Cs^+(15C5)_2Na^-$, $Cs^+(15C5)_2K^-$, Rb^+-$(15C5)_2Na^-$, $Rb^+(15C5)_2Rb^-$, and $Cs^+(15C5)_2e^-$, from 80 to 200 K a shift of the diffraction peaks to low angle is observed that corresponds to a slight change of the cell parameters. This is reversible except in the case of $Cs^+(15C5)_2e^-$. (3) For K^+-$(15C5)_2Na^-$ and $K^+(15C5)_2K^-$, a phase transition occurs between 80 and 200 K.

The determination of the cell parameters from X-ray powder diffraction data for compounds for which it has been impossible to obtain single crystals can be accomplished for alkalides and electrides when a comparison with similar known compounds is possible. By indexing the diffractograms of known compounds, it is possible to index those of the unknown compounds and to refine the cell parameters. However, to do this, XRD powder patterns of high quality are required and it is not always possible to obtain such data for alkalide and electride compounds.

This technique will prove useful to assess the purity and detect any phase transitions that might occur for these compounds. Temperature studies can give information about thermal motions of the atoms, especially those of the complexant.

Structure of Disodium *trans*-Bis(2,6-pyridinedicarboxylato-*O,N*)platinate(II) Hexahydrate

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As part of our studies on alkane activation by aqueous platinum(II) complexes,[1] we have sought to prepare square-planar chelate platinum complexes where all the ligating atoms are *hard*. Our first test case was the known[2] $[Pt(dipic)Cl]^-$, where dipic = 2,6-pyridinedicarboxylate; this compound in fact does not effect alkane activation, possibly because the pyridine ligand is too soft. In the course of the preparation large crystals of a different complex were obtained; this product appeared to be the same as a secondary product observed by Kostic and was assigned as *trans*-$[Pt(\eta^2\text{-dipic-}O,N)_2]^{2-}$ on the basis of its NMR spectrum.[2] Structures of complexes containing dipic as a *bi*dentate ligand are quite rare—only that of the *protonated* $[RuCl_2(\eta^2\text{-dipicH-}O,N)_2]^-$ has been reported[3]—and structural assignments based only upon NMR spectra for related chelates of platinum[4] have proven to be incorrect;[5] hence, we felt it worthwhile to carry out a crystallographic structure determination.

Experimental Section

Synthesis. A mixture of 0.22 g (1.04 mmol) of disodium 2,6-pyridinedicarboxylate (prepared by neutralizing commercial 2,6-pyridinedicarboxylic acid with NaOH) and 0.20 g (0.52 mmol) of Na_2PtCl_4 (Aesar) in 2 mL of H_2O was stirred under Ar until all solids dissolved and allowed to stand; after 24 h a mixture of yellow prisms and purple needles (0.24 g total) was filtered off. The yellow prisms were separated by hand and recrystallized from H_2O.

^1H NMR (D_2O): δ 8.14, t; δ 7.72, dd; δ 7.53, dd; $^3J_{HH}$ = 7.5 Hz; $^4J_{HH}$ = 1.5 Hz. IR (cm^{-1}, Nujol): 3600 w, 3501 w, 2405 m, 2396 m, 1624 s, 1459 m, 1416 m, 1265 m, 1211 w, 1140 w, 1097 w, 1038 w, 916 w. The elemental analysis agreed best with a dihydrate formula, not the hexahydrate determined crystallographically, presumably indicating partial dehydration in handling; it was necessary to protect the crystals

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