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Gold-197 Mössbauer Analysis of Alkali-Metal–Gold Intermetallics and (2,2,2-crypt-M$^+$)Au$^-$ Compounds: Existence of Au$^-$ in the Solid State

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Gold-197 Mössbauer spectroscopy has been used to investigate the MAu intermetallic system (M = Li, Na, K, Rb, Cs) and the (2,2,2-crypt-M$^+$)Au$^-$ compounds (M = K, Rb, Cs). Of the 1:1 intermetallics only RbAu and CsAu give Mössbauer spectra consistent with gold in a cubic environment, but (2,2,2-crypt-M$^+$)Au$^-$ species (M = K, Rb, Cs; 2,2,2-crypt = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) also have cubic gold environments. Comparison of the isomer shifts for the crypted and uncrypted solids suggests that in RbAu and CsAu considerable electron density is removed from the 5d orbitals on gold. All other alkali-metal–gold alloys show doublet Mössbauer spectra indicating sizable electric field gradients at the gold atoms. Evidence for a new phase of composition MAu$_{1.7}$ (M = K, Rb) is also presented, which appears to contain only one, noncubic, gold site.

Introduction

Over 50 years ago Zintl and co-workers reported the results of electrochemical studies of salts of the post transition metals after titration with sodium–ammonia solution.[1-3] These studies, in conjunction with exhaustive alloy extractions, led to the identification of numerous homopolyatomic anions such as Pb$_9^{4-}$, Sn$_9^{4-}$, Sb$_7^{3-}$, Bi$_5^{3-}$, and Te$_2^{2-}$. In the case of gold, potentiometric titration of Na by AuI in liquid NH$_3$ produced an end point corresponding to a ratio of 1:2 Au:Na. This result was interpreted in terms of the formation of an intermetallic compound. However, the data could just as easily suggest the formation of the auride anion, Au$^-$. Indeed, recent spectroscopic and electrochemical studies on alkali-metal (K, Rb, Cs)–gold solutions in liquid NH$_3$ and ethylenediamine have provided convincing evidence for this species.[4-6] It has also been noted that molten CsAu is an ionic conductor like other liquid ionic salts.[4,7]

In Zintl's original studies of the post-transition-metal anions it was observed that removal of the solvent resulted in either amorphous products or known binary alloy phases, probably because of the greater electron delocalization in, and hence stability of, these phases relative to the polyanions. Addition of a crypting agent to alkali-metal–post-transition-metal extractions in liquid NH$_3$, or ethylenediamine, solution has led to the structural characterization of the Zintl anions Sn$_9^{4-}$, Ge$_9^{4-}$ and Ge$_9^{2-}$, Sn$_5^{2-}$ and Pb$_5^{2-}$, Sb$_7^{3-}$ and Bi$_4^{2-}$ and Te$_3^{2-}$.[8-13] In the case of gold, Burns and Corbett[14] have reported that a colorless solid was obtained when a liquid NH$_3$ solution of KAu and a stoichiometric amount of 2,2,2-crypt was evaporated at low temperatures. The material was unstable above ca. −10 °C, giving metallic gold and other unidentified products, possibly reduced ligand. It was suggested that the solid contained the monoatomic Au$^-$ anion (5d^{10}6s^2). However, the exact nature of the gold in this solid is unknown.

Gold-197 Mössbauer spectroscopy has proved to be a valuable method for the determination of the oxidation state of gold compounds. There is a systematic variation of Mössbauer parameters with oxidation state, and the technique is responsive to both the number and nature of ligands bonded to gold.[15,16] Mössbauer spectroscopy has also proved useful for the characterization of gold cluster compounds.[15] It therefore seemed appropriate to examine the spectrum of the material obtained by Burns and Corbett by ^{197}Au Mössbauer spectroscopy in order to compare the spectrum with that of RbAu and CsAu.[17] These last two intermetallic compounds have the CsCl structure,[18] and ^{197}Au Mössbauer and UV and X-ray photoelectron core- and valence-band spectra have established their ionic nature.[17,19] In view of the paucity of ^{197}Au Mössbauer data on alkali-metal–gold alloys, we have also undertaken an extensive investigation of these systems, thereby enabling comparisons with the previous work on RbAu and CsAu and with the crypted compounds prepared in this study.

Experimental Section

Materials. Elemental gold was obtained from Alfa Inorganics (99.95%) and used as received. Some gold was also obtained from Dr. C. J. L. Lock, of this department, in the form of chloroauric acid, from which elemental gold was obtained by standard procedures.[20] Lithium (Aldrich, 98+%, 0.8% Na), sodium (BDH, 99.8%), potassium (MCB), rubidium (Johnson Mathey, 99.9%), and cesium (Aldrich, 99.95+%) metals were used as received and handled only in a nitrogen-filled (argon for Li) drybox (Vacuum Atmospheres Model DLX or Model HE-43-2). Drybox moisture and oxygen levels were routinely less than 0.01 ppm. 2,2,2-crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) was obtained from Merck and was also used as received. Liquid NH$_3$ (Canadian Liquid Air) was stored over sodium or potassium at −78 °C and distilled directly before use. All other materials were of reagent grade quality.

Preparations. Samples of the (2,2,2-crypt-M$^+$)Au$^-$ (M = K, Rb, Cs) compounds were prepared by the reactions of stoichiometric amounts of the binary alloys and 2,2,2-crypt in liquid NH$_3$ at −20 °C. Both RbAu and CsAu reacted quickly on dissolution of the 2,2,2-crypt, while KAu required at least 24 h for complete reaction. In each case the liquid NH$_3$ solvent was then removed at −30 °C and the resulting solid transferred at low temperatures to the cooled Mössbauer cell inside a drybox. The temperature was never allowed to exceed ca. −30 °C in all manipulations of these compounds because decomposition occurs above −10 °C.[14] After they were loaded, the Mössbauer cells were removed from the drybox and stored, until required, immersed in liquid nitrogen.

The preparations of the binary alloys were accomplished either by direct fusion of the elements at high temperatures followed by quenching and annealing or by reaction of AuCN with the appropriate alkali metal in liquid NH$_3$. In the first procedure, the elements were weighed inside a drybox (with a Mettler AE163 top-loading balance) into a molybdenum crucible, which was subsequently sealed by argon-arc welding and enclosed in a quartz jacket. The elements were allowed to react at ca. 200 °C above the liquidus for the particular composition for 1–2 h and

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quenched to room temperature. When necessary, the intermetallics were subsequently annealed (i.e. β'-LiAu, β_2'-LiAu, NaAu, and KAu) for periods of up to 2 months.[18,21-23] The compositions of all samples were shown to be authentic by X-ray powder photography,[18] with the exception of NaAu (see below).

In the second procedure, AuCN was allowed to react with the alkali metals in liquid NH_3, in a manner similar to that originally used by Zintl and co-workers. AuCn was prepared from $K[Au(CN)_2]$ according to the procedure described by Brauer,[24] while the precursor $K[Au(CN)_2]$ was obtained by dissolution of finely divided gold in cold aqueous KCN with oxygen gas bubbling through the solution. The ^{197}Au Mössbauer data for the prepared AuCN are $\delta = 3.52$ (2) mm s^{-1} relative to Au (2.27 mm s^{-1} relative to Pt source) and $\Delta = 7.84$ (2) mm s^{-1}, in agreement with the literature result.[25] In a typical reaction AuCN (0.40 g, 1.79 mmol) was dissolved in ca. 10 cm^3 of liquid NH_3 at −30 °C and the solution was decanted slowly onto the appropriate alkali metal (3.95 mmol) in ca. 2–3 cm^3 of NH_3 at the same temperature. A 10–20% excess of alkali metal over that required to give Au(1−) was used in all of these reactions to dispose of any residual water on the sides of the glass vessels and to allow for any possible reaction of alkali metal with the NH_3 solvent to give alkali-metal amide.[26] In the case of Na and K, black precipitates of $NaAu_2$ and KAu_2 (subsequently established by X-ray powder photography[18]) formed even in the presence of excess alkali metal in NH_3. If the reactions are not performed slowly, by decanting the AuCN solution onto the alkali-metal solution with constant shaking, then some gold metal will form in addition to $NaAu_2$ or KAu_2. The above reactions also take place at temperatures as low as −50 to −60 °C. After the excess alkali metals were allowed to decompose at ca. −30 °C in liquid NH_3 to give the respective amide and hydrogen, the solutions were decanted from the solids and the latter washed several times with liquid NH_3 to remove any alkali-metal amide or cyanide. For Rb and Cs precipitates did not form but instead solutions of RbAu and CsAu, in the presence of excess alkali metal, were obtained. In a series of reactions these solutions were allowed to stand at various temperatures until the excess alkali metal had decomposed and any reaction of RbAu or CsAu with NH_3, to evolve hydrogen, had also ceased. This generally took ca. 12 h, and in each case solids were produced over this period. These solids were treated as described above for $NaAu_2$ and KAu_2 and examined by X-ray powder photography and in two cases chemically analyzed. Two other reactions involving the solutions of RbAu and CsAu with excess alkali metal in liquid NH_3 were also performed. These solutions were stripped of the solvent at low temperatures (<ca. −50 °C) in an attempt to prepare RbAu and CsAu by an alternative procedure. The results of all of the above reactions are discussed in detail below.

Analyses. Analyses were performed for alkali metal (as base) and gold on samples obtained from the ammonolysis of RbAu and KAu. Weighed samples were decomposed in distilled, deionized water by boiling for a number of hours, and the resulting base was titrated with standard HCl and phenolphthalein as indicator. The gold, formed on decomposition of the sample, was dissolved in the minimum amount of HNO_3–HCl solution, and after removal of excess HNO_3, the metal was precipitated with use of hydrazine hydrochloride,[20] filtered through ashless filter paper, ignited, and weighed. Anal. Found for KAu_n: Au, 88.7 (as the element); K, 10.0 (as the base). Found for $RbAu_n$: Au, 78.7 (as the element); Rb, 20.0 (as the base).

X-ray Powder Photography. X-ray powder diffraction photographs were obtained from samples sealed in 0.3 mm o.d. Lindemann glass capillaries mounted in an 11.46 cm diameter Philips Debye–Sherrer camera employing nickel-filtered Cu Kα radiation ($\lambda(K\alpha) = 1.5418$ Å). Table I lists the *d* values and qualitative relative intensities for the stronger lines in powder photographs of the two new phases KAu_n and $RbAu_n$, obtained from the ammonolysis of KAu and RbAu, respectively.

Mössbauer Spectroscopy. ^{197}Au Mössbauer spectra were recorded with an Elscint MFG-N-5 Mössbauer Function Generator, Elscint MDF-N-5 Driver/Generator, and Elscint transducer operating in the constant-acceleration triangular-waveform mode. The source of 77.4-keV radiation (^{197}Au) was in the form of a disk of Pt-metal foil, enriched to 86% ^{196}Pt, weighing 0.100 g and rolled to a thickness of approximately 0.07 mm. This foil was irradiated, in the McMaster University Nuclear Reactor, for 4–6 h at a neutron flux of approximately 1.5×10^{13} cm^{-2} s^{-1} to produce a source of the ^{197}Au precursor, ^{197}Pt, of 14–20-mCi activity. Two foils originating from the same sample of platinum were used and alternately irradiated. One such source could be used for 3 days after irradiation ($t_{1/2} = 18$ h). The foils were mounted in an aluminum holder with walls of a minimum thickness of 2.5 mm to reduce the β^- field by absorption in the aluminum.

Table I. X-ray Powder Diffraction Data for $KAu_{1.7}$ and $RbAu_{1.7}$

$KAu_{1.7}$		$RbAu_{1.7}$	
d, Å	rel intens[a]	*d*, Å	rel intens[a]
4.95	S	5.2	S
2.94	M	3.00	M
2.84	M	2.86	M
2.75	M	2.64	S
2.50	S	2.47	MS
2.44	M	2.33	S
2.31	VS	2.24	MS
2.19	S	1.98	M
1.94	S	1.90	M
1.745	M	1.805	MS
1.670	M	1.760	M
1.535	S	1.581	S
1.382[b]	S	1.435	MS
1.290	M	1.402	M
1.22[b,c]	M	1.31–1.325[b]	M
1.23[b,c]	M	1.240	M
1.148	M	1.178	M
1.077	M		

[a] Abbreviations: S = strong, M = medium, V = very. Weak lines are not listed. [b] Lines are broad possibly as a result of closely spaced lines. [c] These two lines emerge.

Powdered absorber samples containing 0.05–0.15 g cm^{-2} of ^{197}Au were placed, neat, in 20 mm i.d. threaded Kel-F Mössbauer cells under an atmosphere of rigorously dried nitrogen or argon. Both source and absorber were immersed in liquid helium (4.2 K) in a research cryostat manufactured by the Janis Research Co. The temperature was monitored by means of a calibrated Allen-Bradley 47-Ω, $^1/_4$-W carbon resistor and a Cryogenic Research Co. temperature controller. The transmitted radiation was detected by a Harshaw NaI(Tl) scintillation counter (crystal thickness 6.35 mm). The amplified pulses from the counter were fed to an Elscint Promeda Mössbauer multichannel analyzer operating in the multiscaling mode. The pulse-height window was set so as to minimize the background radiation from the unresolved K-shell X-rays.[27] The velocity scale of each spectrum was calibrated individually, without interuption of the drive sequence, with use of an iron foil absorber and ^{57}Co/Rh source both at ambient (room) temperature mounted on the reverse end of the transducer. The unfolded calibration spectra were computer-fitted to give a linear velocity scale and folding point for the sample spectra. The folded spectra were computer-fitted to either single lines or quadrupole doublets in the Lorentzian approximation. The programs used were written in this department by K. Ruebenbauer.[28] The spectrum of a reference absorber of gold foil, obtained from Ventron Corp., 0.025 mm in thickness, was recorded, several times, at the same velocity sweep range as for the experimental samples.

^{127}I Mössbauer spectra of samples of KI and $[2,2,2\text{-crypt-}K^+]I^-$ were recorded at 4.2 K with use of the same experimental setup as described above. The source of 57.6-keV γ-radiation consisted of $Ca_3{}^{127m}TeO_6$ in $Ca_3{}^{126}TeO_6$[29] containing a total of ~0.035 g of tellurium. This source was prepared from $^{126}TeO_2$ that had been irradiated for 4 months in the nuclear reactor.[30] The absorbers each contained 0.015 g cm^{-2} of ^{127}I and were ground with SiO_2, as an inert packing material, before pressing into the Kel-F cell.

Results and Discussion

The ^{197}Au Mössbauer data for the $(2,2,2\text{-crypt-}M^+)Au^-$ (M = K, Rb, Cs) compounds and alkali-metal–gold intermetallics are given in Table II, together with literature data on RbAu and CsAu.

$(2,2,2\text{-crypt-}M^+)Au^-$ (M = K, Rb, and Cs). Gold-197 Mössbauer spectra have been recorded for RbAu and CsAu in

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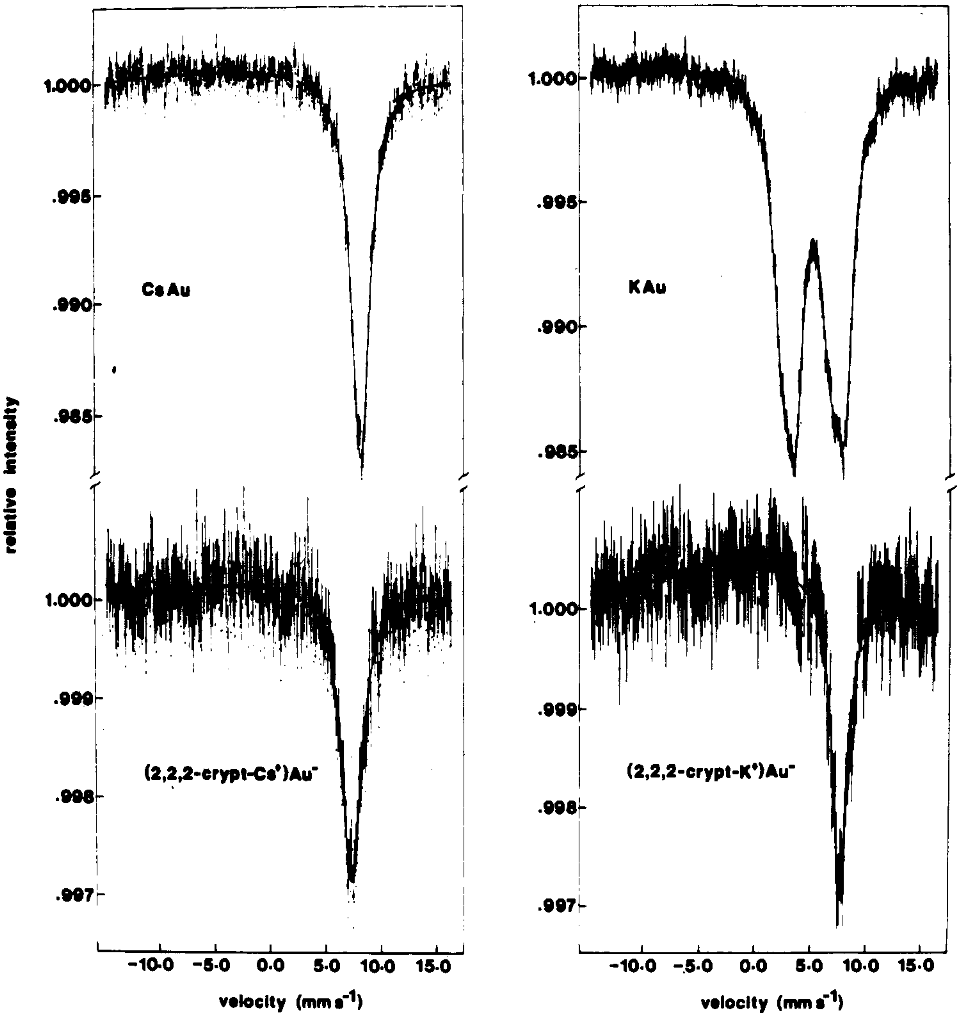

Figure 1. Gold-197 Mössbauer spectra of CsAu, KAu, (2,2,2-crypt-Cs^+)Au^-, and (2,2,2-crypt-K^+)Au^- at 4.2 K.

both previous studies[17] and this study. In each study the spectra of RbAu and CsAu both consist of single, unbroadened resonances with isomer shifts greater than 8 mm s^{-1} with respect to gold metal (Table II). These high isomer shifts, and the properties of the intermetallics, suggest that they have considerable ionic character and could be regarded as salts, M^+Au^-. The outer-electron configuration for Au^- would be $5d^{10}6s^2$ in the limit of complete electron transfer to gold, which accounts for the observed isomer shifts. In fact, the extent of electron transfer to gold has been variously estimated to be from 0.5 to 0.8 e by numerous authors,[17,31,32] and indeed, using Pauling relative electronegativity ideas, one can estimate that RbAu and CsAu have only 47 and 51% ionic character, respectively (cf. CsCl, 74% on the same scale). In these phases the Rb–Au and Cs–Au distances are only 3.56 and 3.69 Å, respectively, certainly suggesting that considerable overlap of M^+ and Au^- orbitals is possible.

Two possibilities for orbital overlap arise that would have opposite effects on the total s-electron density at the gold nucleus and hence would affect the Mössbauer isomer shifts differently. In Rb^+Au^- and Cs^+Au^-, if the filled 5d level on gold does interact strongly with the empty orbitals on the alkali metal, a deshielding of the gold 6s electrons would result. An increase in s-electron density would follow and produce an increase in isomer shift relative to the case when no orbital interaction occurs. In fact, it has been estimated that complete removal of one 5d electron would result in a shift of ~+1 mm s^{-1} for these MAu compounds.[17] However, these same authors have measured the XPS valence band spectrum of CsAu and conclude that the Au 5d level is too low in energy for significant withdrawal of d electrons to occur, being some 7 eV below the Fermi level. (They actually estimate a net charge transfer of 0.7 ± 0.1 e.) If this latter case is the situation, then isolation of the Au^- anion with a filled 6s shell and a full complement of 5d electrons should produce an even higher Mössbauer isomer shift than has been observed.[17]

An increase in the cation–anion distance and a decrease in their interaction can be achieved by encapsulating the cation in a crypting agent such as 2,2,2-crypt. We have treated the stoichiometric 1:1 intermetallics KAu, RbAu, and CsAu with 2,2,2-crypt in liquid NH_3 at −20 °C and obtained colorless solutions. These solutions are stable for at least 3 months when kept at −70 °C, but they decompose slowly at higher temperatures. Removal of the solvent at low temperature results in solids, which are also stable if kept cold. Gold-197 Mössbauer spectra were recorded for these crypted intermetallics, and the data are given in Table II. The spectra for KAu and CsAu both before and after the crypting of the cation are shown in Figure 1. The spectrum of KAu consists of two absorptions, the origin of which will be discussed in detail below. The Rb and CsAu intermetallics give single lines, as noted above, with isomer shifts that agree well with previously reported values (Table II). After treatment with 2,2,2-crypt KAu, RbAu, and CsAu all give single-resonance absorptions, indicating that the gold is in a symmetric environment, and the isomer shifts are ~7.4 mm s^{-1}. In the potassium case the crypting process results in a considerable increase in isomer shift, and hence s-electron density, but for the rubidium and cesium cases there is a decrease in the isomer shift, meaning that the s-electron density has been reduced. Since the act of separating the cation from the anion would not result in the transfer of gold 6s electrons to the alkali metal, we conclude that the lower s-electron density results from a higher 5d-electron density on the gold atoms, and hence an increased shielding of s electrons. It

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Table II. ^{197}Au Mössbauer Data for Alkali-Metal–Gold Compounds

		δ, mm s^{-1} [a]	Δ, mm s^{-1}	fwhm, mm s^{-1} [b]	rel contribn of site	ref
(2,2,2-crypt-Cs)Au		7.34 (5)		2.2 (2)		
(2,2,2-crypt-Rb)Au		7.34 (4)		2.0 (1)		
(2,2,2-crypt-K)Au		7.55 (5)		1.8 (1)		
CsAu		8.22 (2)		2.01 (5)		
CsAu		8.35 (6)		2.06		17
RbAu		8.00 (3)		1.93 (7)		
RbAu		8.07 (1)		2.06		17
$RbAu_n$ [c]		4.52 (2)	4.41 (2)	2.16 (3)		
KAu	site 1	4.39 (5)	4.32 (4)	1.7 (1)	0.29	
	site 2	5.64 (4)	4.46 (2)	2.12 (7)	0.71	
KAu_n [d]		4.40 (2)	4.31 (1)	2.43 (3)		
KAu_2	site 1	3.13 (3)	3.45 (1)	2.26 (4)	0.82	
	site 2	4.10 (6)	3.95 (6)	2.0 (1)	0.18	
KAu_2 [e]	site 1	3.26 (2)	3.22 (4)	2.31 (4)	0.85	
	site 2	3.56 (5)	5.1 (1)	1.9 (1)	0.15	
"NaAu" [f]		5.32 (2)	4.24 (1)	2.12 (3)		
$NaAu_2$ [g]		3.02 (1)	3.67 (1)	2.66 (2)		
LiAu		4.57 (1)	2.69 (1)	2.64 (2)		
$Li_{1.1}Au_{0.9}$	site 1	4.88 (1)	2.61 (2)	2.64 (2) [h]	0.78	
	site 2	4.93 (2)			0.22	

[a] Isomer shifts relative to Au metal. [b] Full width at half-maximum. [c] $RbAu_n$: $n = 1.7$ (1) (chemical analysis). [d] KAu_n: $n = 1.7$ (1) (chemical analysis). [e] Alternate choice of parameters for KAu_2. [f] "NaAu" = Au-rich component from mixture obtained from reaction of Na and Au in the melt, annealed 2 months (see text). [g] $NaAu_2$:GK_{11} = 1.11 (1). [h] Line widths constrained to be equivalent for the two sites.

would appear then that in RbAu and CsAu about 0.75–0.88 electron is removed from the Au 5d orbital on the basis of the estimate of ~1 mm s^{-1} change in isomer shift for removal of one 5d electron. Such an extensive reduction in the electronic complement of the 5d level would seem to be in conflict with the XPS valence-band data on CsAu, and most likely the above estimate of ~1 mm s^{-1} is a little small. Also not considered in this analysis would be an intrinsic difference between the CsCl structure of CsAu and RbAu and the (presently unknown) structure(s) of the (2,2,2-crypt-M^+)Au^- salts. Suffice it to say that while in the limit CsAu and RbAu may be considered as ionic with considerable charge transfer to gold from the alkali metals, ^{197}Au Mössbauer investigation indicates that there has been some reduction in the 5d electronic complement on gold.

Further evidence that the act of crypting the cation reduces the M^+–Au^- Coulombic interaction comes from a comparison of the recoil-free fractions of MAu and (2,2,2-crypt-M)Au. For equal amounts of gold the recoilless fraction of the crypted salt is 1 order of magnitude smaller than for the uncrypted intermetallic. The lower Coulombic interaction in the crypted case would result in a much lower Debye temperature and hence a lower percentage absorption. To test this conclusion, we recorded the ^{127}I Mössbauer spectra of the ionic salt KI and (2,2,2-crypt-K)I. In this case the absorption of the crypted KI was ~5 times smaller than for pure KI. The smaller effect observed for ^{127}I on crypting is consistent with the energies of the γ transition for the two nuclei. Since the recoilless fraction is proportional to $e^{-E_\gamma^2}$, and $E_\gamma = 77.4$ keV for ^{197}Au and 57.6 keV for ^{127}I, the ^{197}Au absorption would be most affected by the action of crypting the salt. No detectable difference in ^{127}I isomer shift was observed on crypting the KI. However, this is not too surprising since KI is largely ionic in nature, and furthermore, the $\delta R/R$ term is small for ^{127}I so that small changes in s-electron density would be difficult to detect.

Alkali-Metal–Gold Intermetallics. The phase diagrams for the M–Au system (M = Li, Na, K, Rb, Cs) all show a stable phase at, or close to, the 1:1 stoichiometry.[18] Both CsAu, bright yellow, and RbAu, yellow-brown to bronze, have been well-characterized and adopt the CsCl-type crystal structure (CsAu, $a = 4.26$ Å; RbAu, $a = 4.11$ Å).[33] The gold atoms are in cubic environments, and hence the ^{197}Au Mössbauer spectra should appear as unsplit absorptions, as has been observed.[17] Our results agree well with the literature data. When M = Li, Na, K, the MAu alloys take on a metallic luster and these are clearly different from the rubidium and cesium intermetallics discussed above. X-ray powder diffraction studies[18] have shown that KAu and NaAu do not have the CsCl-type lattice. The patterns are quite complex, suggesting low symmetry, and they have not been indexed so that no structural data are available for these intermetallics.

The ^{197}Au Mössbauer spectrum of KAu consists of two lines of equal area and is quite different from those of either CsAu or RbAu (Figure 1). The two absorptions could arise from two different gold sites having isomer shifts of ~3 and ~7 mm s^{-1}, respectively. While the line at ~7 mm s^{-1} might reasonably be interpreted as arising from a potassium–gold intermetallic, that at ~3 mm s^{-1} would be more difficult to account for. A computer fit to two independent Lorentzian lines turns out to be rather poor. The non-Lorentzian shape of each line leads us to the conclusion that this spectrum is best interpreted in terms of two overlapping quadrupole-split doublets with contributions of 29 and 71%. The isomer shifts of the two sites are considerably lower than those of ionic CsAu and RbAu and are consistent with the more metallic nature of KAu, notwithstanding the change in structural type. The isomer shifts are in the range observed for AuMn and $AuMn_3$,[34] $AuIn_2$ and $AuGa_2$,[35,36] AuMg,[17] and the ternary intermetallics reported by Gütlich et al.[37] The fairly large quadrupole splittings are consistent with the apparent lower symmetry of the gold in KAu compared to that in cubic CsAu and RbAu as noted above. These large splittings are unusual for gold intermetallics,[37,38] where, except for $AuTe_2$,[39] none have heretofore been observed. In $AuTe_2$, the quadrupole splitting is 2.29 mm s^{-1} and Au–Te distances are four at 2.68 Å and two at 2.97 Å.[40] Since the quadrupole splittings in KAu are twice as large as this, the gold environments must be considerably more distorted. It is quite likely that such large splittings could result from Au–Au interactions and therefore could be an indication of clustering in this phase.

Attempts to prepare a pure sample of NaAu were unsuccessful. Examination of the Na–Au phase diagram[18,22] shows that, for the composition NaAu, there is a difference of ca. 500 °C between the liquidus and the peritectic formation temperature (372 °C) of solid NaAu (cf. KAu, for which the difference is only 115 °C). Even annealing a quenched sample of this composition at 365 °C for 2 months had little effect, and X-ray powder diffraction photographs indicated the presence of $NaAu_2$ (as expected from the phase diagram) as well as a pattern from at least one other phase. After the X-ray powder diffraction pattern of $NaAu_2$ was accounted for, the remaining pattern showed some similarity to that reported for NaAu although some lines were absent. No Na_2Au could be detected. This suggests that either another phase not previously reported in the NaAu system is present or, less likely, the X-ray powder data for NaAu are in error. The ^{197}Au Mössbauer spectrum of this annealed sample was fitted to two quadrupole-split doublets of differing intensity. The more intense doublet was subsequently found to be due to $NaAu_2$. The second quadrupole-split doublet therefore arises from a more sodium-rich phase, possibly NaAu. The isomer shift of this latter doublet is slightly lower than that of the high-isomer-shift doublet in the spectrum of KAu. This is consistent with the lower electropositivity of sodium compared to that of potassium. However, the X-ray powder diffraction data show that the structure of this phase

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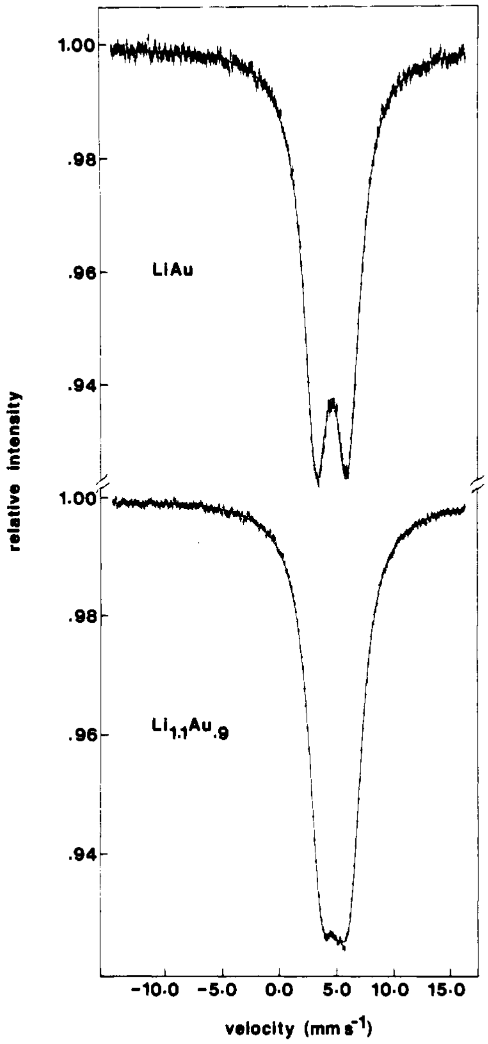

Figure 2. Gold-197 Mössbauer spectra of LiAu and $Li_{1.1}Au_{0.9}$ at 4.2 K.

(NaAu) is certainly different from that of KAu. The quadrupole splitting is very similar to those found for the two sites in KAu, again consistent with noncubic symmetry for gold in this phase.

The Li–Au system exhibits a complex phase diagram[18,22] with the LiAu phase existing over the composition range of ca. 44–53 atom % Au. Within this range three related structural forms have been found. From 44 to 45 atom % Au the structure is cubic (β'), with the CsCl-type lattice ($Pm3m$, $a = 3.098$ Å; 0.9 Au + 0.1 Li at 0, 0, 0 and 1.0 Li at $^1/_2$, $^1/_2$, $^1/_2$). At 46 atom % Au the structure is tetragonal, β_1' ($a = 3.23$ Å, $c = 2.83$ Å), while at 48.2 atom % Au the structure is orthorhombic, β_2' ($a = 3.30$ Å, $b = 3.21$ Å, and $c = 2.80$ Å with the a/b ratio increasing with increasing gold content). An orthorhombic (β_2') form with 50 atom % Au and the cubic β' form (44.5 atom % Au) were investigated by ^{197}Au Mössbauer spectroscopy, and the resulting spectra are shown in Figure 2. The composition LiAu (β_2') exhibits a quadrupole-split doublet as expected for the reduced symmetry. The isomer shift is lower than those found for the other stoichiometric 1:1 phases in keeping with the lower electropositive character of lithium. The ^{197}Au Mössbauer spectrum of the cubic β' form, with composition $Li_{1.1}Au_{0.9}$, is somewhat more difficult to interpret. Although β' is cubic with a CsCl-type lattice (8:8 coordination), the gold site at 0, 0, 0 contains 10% lithium, leading to a lowering of cubic symmetry about much of the gold in the alloy. A disordered distribution of the 10% Li on the Au sites leads to a broad range of differing environments for neighboring Au atoms from cubic to much lower symmetries, thus giving rise to a singlet as well as a variety of small quadrupole splittings in the Mössbauer spectrum. The ^{197}Au Mössbauer spectrum for the β' form was fitted to two overlapping spectra, one a singlet and the other a doublet, giving experimentally determined contributions of 22 and 78%, respectively. The isomer shift values of the two sites are within 3σ of each other and are also fairly similar to that of LiAu. In addition, the quadrupole splitting for the major site of $Li_{1.1}Au_{0.9}$ is almost identical with that of LiAu. Interestingly, the quadrupole splittings of both are substantially less than those obtained for the two sites of KAu and that of "NaAu". Thus, the environments about gold in KAu and "NaAu" must be much more distorted from cubic symmetry than either $Li_{1.1}Au_{0.9}$ or LiAu, which are derived from a CsCl-type lattice or small distortions of the same. One final point of interest concerns the reappearance of the CsCl-type lattice in the Li–Au system. Both ionic CsAu and RbAu satisfy the packing considerations for the CsCl lattice as embodied in the radius ratio concept, i.e. $r_+/r_- > 0.73$ (CsAu, $r_+/r_- = 0.902$; RbAu, $r_+/r_- = 0.775$; Ladd ionic radii used for Cs^+ and Rb^+). However, KAu, NaAu, LiAu, and $Li_{1.1}Au_{0.9}$ are metallic in nature and should not satisfy these conditions. In the case of lithium, the least electropositive of the alkali metals, the ratio of the metallic radii $r_{Li}/r_{Au} = 1.041$ falls within the domain of the CsCl-type lattice. Thus, CsAu and RbAu adopt the cubic CsCl-type lattice, but with decreasing electropositive nature of the alkali metals the onset of metallic character appears and noncubic structures are formed. With $Li_{1.1}Au_{0.9}$, the metallic character has increased sufficiently, through charge equalization, to allow the CsCl-type lattice to appear once again. Indeed, a body-centered cubic structure related to the CsCl structure is very common amongst metals, most notably in the present case for the alkali metals themselves.

Reduction of AuCN by the Alkali Metals in Liquid Ammonia. With the failure to obtain NaAu by the direct reaction of the elements as discussed above, an alternative method of preparation was investigated involving reduction of AuCN by sodium in liquid NH_3 according to eq 1. The reactions of the other alkali metals,

$$AuCN + 2M \rightarrow MAu + MCN \qquad (1)$$

$$M = Na, K, Rb, Cs$$

except Li, were also studied by this method. Gold(I) cyanide is quite soluble in liquid NH_3, and the reactions were conveniently carried out at −30 °C or lower. Somewhat surprisingly, the reactions of sodium and potassium with AuCN did not produce the expected NaAu and KAu, but rather the less reduced alloys $NaAu_2$ and KAu_2. Attempts to reduce the latter alloys with large excesses of the appropriate alkali metal were unsuccessful. In these reactions the alloys presumably act to catalyze the reactions of the alkali metal with NH_3 to give alkali-metal amide and hydrogen, as is well-known for finely divided metals.[26]

The ^{197}Au Mössbauer spectra of $NaAu_2$ and KAu_2 are shown in Figure 3. These two spectra are very similar, each consisting of two lines, the area of each accounting for precisely 50% of the spectral intensity. In both cases the higher velocity peak is broader than the other peak (2.59 (4) and 2.74 (4) mm s^{-1}, $NaAu_2$; 2.43 (2) and 2.71 (3) mm s^{-1}, KAu_2) and is of correspondingly lower maximum amplitude. These factors lead us to conclude that, similarly to the spectrum of KAu, each of these two spectra arises from two (or more) quadrupole-split spectra of similar isomer shift, rather than from two (or more) unsplit spectra of considerably different isomer shift, and therefore effectively different oxidation states for the Au atoms.

Close examination of the spectrum of KAu_2, and simulations thereof, reveals a slight asymmetry in the profile of the higher velocity peak indicating a weaker component under its high-velocity flank. This spectrum was therefore satisfactorily fitted to two quadrupole sites of unequal contribution (see Table II). The resultant fit gives, visually, better agreement with the experimental data than do fits to (i) two single Lorentzian lines, (ii) one quadrupole site (with or without preferred orientation or Goldanskii–Karyagin effects), or (iii) two quadrupole sites of equal contributions. Unfortunately, since the lower velocity peak in the KAu_2 spectrum does not show any noticeable asymmetry, the relative velocity of the low-velocity components of the two quadrupole doublets cannot be discerned unambiguously. Consequently, it was found that convergence on either of two models (1 and 2 in Table II) occurs. A slight preference of model 1 might

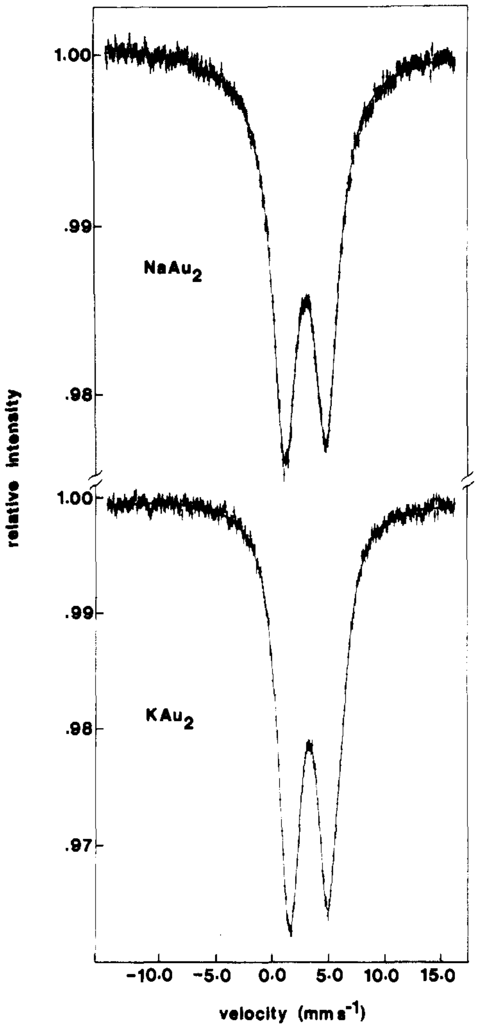

Figure 3. Gold-197 Mössbauer spectra of $NaAu_2$ and KAu_2 at 4.2 K.

be expressed upon the basis of an assumption that the quadrupole splittings and isomer shifts will have a positive correlation. This model also yields parameters for the weaker site that are more comparable with those of the new phase $KAu_{1.7(1)}$ discussed below.

For $NaAu_2$ no asymmetry in the shape of either peak in the spectrum can be detected. Attempts to fit this spectrum to two quadrupole sites did not result in convergence without arbitrary constraints to the relative contributions of the two sites. The best agreement to the experimental data was found for a single quadrupole site with compensation for the unequal amplitudes of the two peaks by either Goldanskii–Karyagin or preferred-orientation effects. The data from this fit are included in Table II. However, it is probable that two gold environments are present in this system.

As indicated above, the reactions of sodium and potassium with AuCN gave $NaAu_2$ and KAu_2, respectively. In order to establish the composition of the most reduced intermetallic in the K–Au system that is stable in liquid NH_3, a sample of KAu was treated with liquid NH_3 at room temperature. The Na–Au system could not be investigated by this means because pure NaAu could not be obtained as noted above. Repeated washing with liquid ammonia under the above conditions resulted in the extraction of potassium and its oxidation by NH_3 to give KNH_2 and H_2. After isolation, the blue-gray metallic residue produced was found to have the composition $KAu_{1.7(1)}$ by chemical analysis. The X-ray powder pattern of this material showed no evidence for either KAu or KAu_2 (Table I), the only known phases in the K–Au system around this composition. However, the pattern of intensities did show some similarity to that of KAu_2, suggesting a similar heavy-atom distribution in these materials. The ^{197}Au Mössbauer spectrum is reproduced in Figure 4 and consists of a single quadrupole-split doublet. Thus the ^{197}Au Mössbauer spectra and the X-ray powder diffraction data suggest that this is a new phase in the K–Au system, but one not accessible by the high-temperature synthetic route. Possible candidates include K_2Au_3, K_3Au_4, and K_3Au_5, but the errors in the analysis preclude any choice between these (or other similar) possibilities. The isomer shift and quadrupole splitting are both greater than those of either of the sites found for KAu_2 but are, interestingly, very similar to those of the site in KAu with the lower isomer shift. This suggests, not unreasonably, that in a series of intermetallics of similar composition in a particular system, the same or very similar sites will contribute to two different alloy compositions.

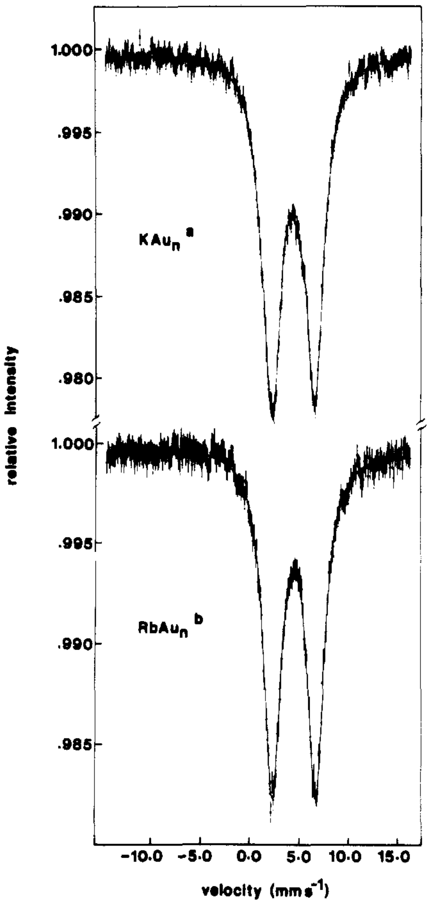

Figure 4. Gold-197 Mössbauer spectra of KAu_n and $RbAu_n$ at 4.2 K: (a) product from the reaction of KAu with liquid NH_3 at room temperature (n = 1.7 (1) (chemical analysis)); (b) residue from the reaction of excess Rb with AuCN and liquid NH_3 at approximately −60 °C.

Reaction of rubidium and cesium with AuCN at −30 °C, or lower, in liquid NH_3 produced the expected products, RbAu and CsAu, respectively, as indicated by eq 1. The presence of these two products was unmistakable, on the basis of the colors of the solids obtained when the solutions were splashed around the ampules. The difference in behavior of these two reactions, compared to the reactions of AuCN with sodium and potassium, presumably results from the ionic nature of RbAu and CsAu, which are soluble in liquid NH_3, whereas $NaAu_2$ and KAu_2 would appear to be very stable and insoluble compounds. The solutions of RbAu and CsAu in liquid NH_3 are not stable for extended periods, even in the presence of excess alkali metal, particularly at higher temperatures. In order to obtain samples containing RbAu and CsAu by this alternative procedure for the purpose of ^{197}Au Mössbauer spectroscopic analysis, and to compare these spectra with those obtained previously, solutions of these compounds in liquid NH_3 were stripped of solvent at low temperatures (<ca. −50 °C). Since no intermetallics of composition M_2Au are known in either system, the presence of excess alkali metal, or of alkali-metal cyanide, was not expected to influence the resulting ^{197}Au Mössbauer spectra. Interestingly, while the ^{197}Au Mössbauer spectra of the resulting solids indicated the presence of CsAu, with an isomer shift identical with that obtained previously (Table II), a quad-

rupole-split doublet was observed in the rubidium system. This is shown in Figure 4b. The corresponding X-ray powder diffraction data indicated the presence of CsAu and CsCN in the cesium system, and RbCN and a pattern different from that of any of the known phases in the Rb–Au system (RbAu, $RbAu_2$, and $RbAu_4$). The identity of this phase will be discussed below.

As noted above, solutions of RbAu and CsAu in liquid NH_3 are unstable over prolonged periods of time, even in the presence of excess alkali metal. Hydrogen is generated, and in both cases solids form. Solutions of CsAu and RbAu were therefore allowed to decompose at room temperature, and another containing RbAu was allowed to decompose at −30 to −40 °C. The ^{197}Au Mössbauer spectra of the products in the rubidium system were somewhat complicated. For the solution allowed to decompose at room temperature, the spectrum consisted of a single line with an isomer shift identical with that of gold metal and a quadrupole-split doublet, with contributions of 37.3 and 62.7%, respectively. The isomer shift and quadrupole splitting for the doublet were identical with those for the phase obtained on stripping the solvent from a solution of RbAu, in the presence of rubidium, at −50 °C. The solution allowed to decompose at −30 °C gave a solid product for which the ^{197}Au Mössbauer spectrum was dominated by the same quadrupole doublet as above but was further complicated by at least two components at lower isomer shift, which may account for up to 30% of the spectral intensity. Lack of resolution, and of a suitable model, prevent unambiguous assignment of parameters for these components. In either case, X-ray powder photographs showed only the presence of the pattern attributable to the phase obtained on stripping the solvent from an RbAu solution at low temperatures. This would suggest that little elemental gold is actually present in the samples obtained after decomposition at room temperature or low temperature, unless it is in an amorphous form. Also, because of the higher recoil-free fraction of elemental gold compared to the alkali-metal–gold phases studied in this work the relative contribution of the gold metal resonance to the ^{197}Au Mössbauer spectra of these samples would exceed the actual relative abundance of gold metal. Chemical analysis of the solid obtained on decomposition at room temperature indicated a composition of $RbAu_{1.7(1)}$, in apparent agreement with the composition of the K–Au phase obtained in a related reaction described above. Even if 30% of the gold in this sample were present as elemental gold, the remaining intermetallic would still possess a composition intermediate between RbAu and $RbAu_2$. It would appear, therefore, that just as was found for the K–Au system, a new and perhaps similar phase exists in the Rb–Au system that lies between RbAu and $RbAu_2$. The ^{197}Au Mössbauer spectra for the two systems (Figure 4) yield parameters (Table II) that are closely comparable; the potassium intermetallic gives the lower isomer shift, consistent with the relative electronegativities of the alkali metal. Moreover, their X-ray powder diffraction patterns, although not indicating isomorphicity, were strikingly similar. These phases appear to be inaccessible by a high-temperature synthetic method.

In the cesium system the sole product from decomposition of the NH_3 solution of CsAu at room temperature, detectable by X-ray powder photography, was gold metal. The ^{197}Au Mössbauer spectrum showed an intense single line whose isomer shift is identical with that for pure gold but also contained a very weak signal, <10% of the total spectral intensity, centered at approximately 6.4 mm s^{-1} relative to elemental composition between that of Au and CsAu. No such phases are reported in the binary phase diagram for the Cs–Au system.[18,22] Earlier workers[17] have also detected a resonance between those for Au and CsAu (at approximately 2.3 mm s^{-1} relative to gold) when recording the spectrum of an impure sample of CsAu. It is possible that these weak signals represent the two components of a quadrupole doublet analogous to those found by us for the intermediate phases in the K–Au and Rb–Au systems. Since this intermediate CsAu phase is a minor component in either the spectrum of CsAu[17] or in that resulting from oxidation by NH_3 of CsAu, one of the components of the postulated quadrupole doublet would be concealed by the flanks of either the Au or the CsAu resonances. We find that a component with parameters δ = 4.0 (1) mm s^{-1} and Δ = 4.6 (2) mm s^{-1} gives the best agreement with our experimental data. However, it appears that any phases intermediate between Au and CsAu are much less stable and more susceptible to oxidation to gold metal than are analogous phases in the rubidium and potassium systems.

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Synthesis and Redox Properties of a Bipyridyl Analogue of Ruthenium Red

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The preparation of the new compound bis[(μ-oxo)-*cis*-aquabis(bipyridine)ruthenium]-*trans*-bis(bipyridine)ruthenium(6+) perchlorate, with the formula $[(bpy)_2(H_2O)Ru^{III}ORu^{IV}(bpy)_2ORu^{III}(OH_2)(bpy)_2](ClO_4)_6$ (bpy = 2,2′-bipyridyl), is reported. Cyclic, differential-pulse, and rotating-disk-electrode voltammetric studies in aqueous solution over the pH range −0.16 to 13.9 reveal seven distinct valence states from [II,II,II] to [IV,V,IV]. The isolated [III,IV,III] complex has acid dissociation constants with pK_a values of 5.0 and 6.8 as determined by glass-electrode titration. Dissociation constants are also reported for other valence states as inferred from the formal reduction potential vs. pH plot. XPS data on the complex reveal peaks at 281.3 and 287.6 eV, which are believed to be due to Ru $3d_{5/2}$ and Ru $3d_{3/2}$ transitions, respectively. The UV–visible spectra of the complex in acidic and basic solutions are presented. In acid, the visible spectrum is dominated by a peak at 649 nm, $\epsilon = 1.04 \times 10^5$ M^{-1} cm^{-1}. The data on the new compound are compared to data on the water oxidation catalyst $[(bpy)_2(OH_2)RuORu(OH_2)(bpy)_2]^{4+}$ and $[(NH_3)_5RuORu(NH_3)_4ORu(NH_3)_5]^{6+}$ (ruthenium red).

Introduction

A remarkable redox chemistry is being uncovered for the aqua and oxo polypyridyl complexes of ruthenium.[1] The monomer $[Ru^{II}(bpy)_2(OH_2)_2]^{2+}$ (bpy = 2,2′-bipyridyl) and the dimer $[(bpy)_2(H_2O)Ru^{III}ORu^{III}(H_2O)(bpy)_2]^{4+}$ each show several higher oxidation states.[2,3] The Ru–bpy dimer (as we will refer to it for

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