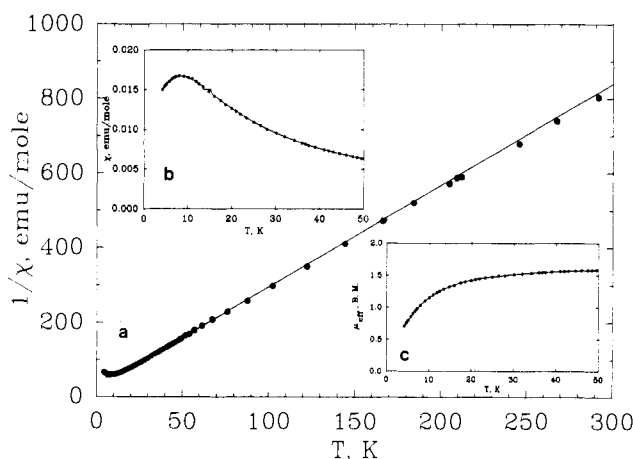


**Figure 3.** Thermal analysis curves (weight loss and DTA) for VOHPO<sub>4</sub>·4H<sub>2</sub>O obtained in flowing He at 10 °C/min heating rate.



**Figure 4.** Magnetic susceptibility data for polycrystalline VOHPO<sub>4</sub>·4H<sub>2</sub>O: (a) inverse susceptibility vs  $T$  (4–300 K); (b) susceptibility vs  $T$  (4–50 K); (c) effective magnetic moment vs  $T$  (4–50 K). The smooth curves represent a fit to the Bonner and Fisher linear-chain model, eq 1, with  $J = -4.5 \text{ cm}^{-1}$  and  $g = 1.98$ .

These experiments suggest that the exotherm near 700 °C is associated with crystallization of an amorphous precursor to vanadyl diphosphate. The sharp endothermic peak at 1239 K corresponds to the melting point of authentic (VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub>.<sup>10</sup> A small endothermic feature at about 1210 K is associated with the melting temperature of V<sup>III</sup><sub>2</sub>(VO<sup>2+</sup>)<sub>2</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>.<sup>11</sup>

Magnetic susceptibility data, obtained at 6 kOe and corrected for ligand diamagnetism ( $-95 \times 10^{-6}$  cgsu), for polycrystalline VOHPO<sub>4</sub>·4H<sub>2</sub>O, are shown in Figure 4. A plot of inverse corrected susceptibility vs temperature (Figure 4a) is linear above 25 K. The susceptibility curve (Figure 4b) has a broad maximum at about 8 K. The effective magnetic moment (Figure 4c) decreases from 1.78  $\mu_B$  at about 300 K to 0.75  $\mu_B$  at 4.2 K. Attempts to fit these data to the HDVV exchange coupled dimer model gave unacceptable values of  $J$  and  $g$ . A better fit, shown in Figure 4, is obtained by using a numerical representation<sup>12</sup> (eq 1, where  $x = |J|/kT$ ) of the Bonner and Fisher  $S = 1/2$  linear-chain model<sup>13</sup>

$$\chi_M = (Ng^2\mu_B^2/kT)(0.25 + 0.14995x + 0.30094x^2) / (1.0 + 1.9862x + 0.68854x^2 + 6.0626x^3)^{-1} \quad (1)$$

(10) Wroblewski, J. T., unpublished observation.

(11) The compound V<sup>III</sup><sub>2</sub>VO(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub> was prepared by reaction of VOHPO<sub>4</sub>·4H<sub>2</sub>O with water-saturated N<sub>2</sub> at 1100 °C. The single-crystal structure of this mixed-valent trimer has been determined: Wroblewski, J. T.; Thompson, M. R., manuscript in preparation.

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with the Hamiltonian in eq 2. Best fit parameters are  $J = 4.5$

$$H = -2J\sum(S_i^z S_{i+1}^z + S_i^x S_{i+1}^x + S_i^y S_{i+1}^y) \quad (2)$$

$\text{cm}^{-1}$  and  $g = 1.98$ . Paramagnetic impurity and interchain exchange corrections to eq 1 are unnecessary within experimental uncertainty.

The experimental results for VOHPO<sub>4</sub>·4H<sub>2</sub>O described above are consistent with the single-crystal structure of Leonowicz et al.<sup>1</sup> Repeated attempts to isolate VOHPO<sub>4</sub>·0.5H<sub>2</sub>O as an intermediate in the VOHPO<sub>4</sub>·4H<sub>2</sub>O to (VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub> transformation were unsuccessful: VOHPO<sub>4</sub>·0.5H<sub>2</sub>O could only be obtained by dehydration of the tetrahydrate to an amorphous vanadium phosphate followed by hydrothermal reaction (Experimental Section). Thus, although the structures of VOHPO<sub>4</sub>·4H<sub>2</sub>O, VOHPO<sub>4</sub>·0.5H<sub>2</sub>O, and (VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub> are related, there is no direct evidence to support the intermediacy of the hemihydrate in the solid-state decomposition of the tetrahydrate to the diphosphate.

**Acknowledgment.** Powder X-ray diffraction patterns were obtained by Frank L. May. John J. Freeman collected Raman and IR spectral data. Thermal analyses were performed by Deborah A. Carter.

**Supplementary Material Available:** Tables of observed and calculated X-ray powder diffraction data for VOHPO<sub>4</sub>·4H<sub>2</sub>O and VOHPO<sub>4</sub>·0.5H<sub>2</sub>O (3 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Inorganic Chemistry, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands, and University of Minnesota, Minneapolis, Minnesota 55455

#### Separation of Cationic Metal Cluster Compounds by Reversed-Phase HPLC

Wim Bos,<sup>†</sup> J. J. Steggerda,<sup>\*†</sup> Shiping Yan,<sup>‡§</sup> Joseph A. Casalnuovo,<sup>†</sup> Ann M. Mueting,<sup>†</sup> and Louis H. Pignolet<sup>\*†</sup>

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High-performance liquid chromatography (HPLC)<sup>1</sup> has been used as a standard technique in organic chemistry for many years. It has only been in the last few years, however, that HPLC has been recognized to be equally useful in inorganic chemistry. A number of HPLC separations of neutral mononuclear compounds or cluster compounds have been reported.<sup>2–7</sup> For the separation of mononuclear cationic complexes, new techniques such as ion-pairing chromatography have been introduced.<sup>8–13</sup> No standard methods, however, have been developed for the separation of cationic metal cluster compounds. Because our research groups have been synthesizing a wide variety of cationic metal clusters in the last few years,<sup>14–23</sup> we have begun to utilize HPLC for the separation and identification of these compounds. A wide variety of large cationic metal cluster compounds have been successfully separated by this technique. In this report we present some of our achievements in this area.

#### Experimental Section

Gold cluster compounds were prepared according to the literature.<sup>24–30</sup> The osmium-gold,<sup>31</sup> ruthenium-gold,<sup>21,23</sup> rhenium-gold,<sup>20,22</sup> and platinum-gold<sup>20,32,33</sup> clusters were obtained by procedures previously described.

**Gold Cluster Compounds.** The HPLC separations were performed with a modular LKB liquid chromatographic system consisting of a 2150 HPLC pump, 2152 controller, 2158 Uvicord SD detector operated at 254

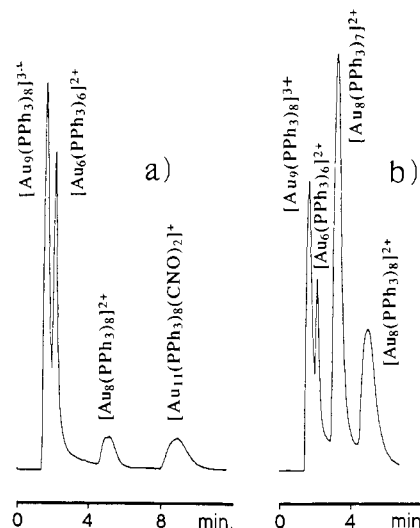
<sup>†</sup> University of Nijmegen.

<sup>‡</sup> University of Minnesota.

<sup>§</sup> Visiting scientist from Nankai University of Tianjin, China.

nm, and a 2156 solvent conditioner along with a 7125 Rheodyne injector, all obtained from LKB. Column: two Chrompack Chromspher C18 glass cartridges (100 × 3 mm) were coupled to a 200 × 3 mm column. Eluent: a helium-degassed 335/120/1 solvent mixture of C<sub>2</sub>H<sub>5</sub>OH, H<sub>2</sub>O, and NH<sub>4</sub>NO<sub>3</sub> (w/w) was used isocratically. Flow rate: 0.70 mL/min. A type A Chrompack guard column filled with pellicular reversed-phase material was used. The aforementioned columns were directly purchased from Chrompack. Preparative column: Lobar prepac HPLC column (310 × 25 mm) obtained from Merck.

**Os-Au, Ru-Au, Re-Au, and Pt-Au Cluster Compounds.** The HPLC separations were performed with a modular Rainin liquid chromatograph consisting of three Rabbit-HPX pumps with pressure module and dynamic solvent mixer, a Knauer variable UV detector operating at 254 nm, and a 7125 Rheodyne injector. The system was controlled by an Apple Macintosh computer with Rainin software. Column: Dynamax 60-Å, 8-μm (250 × 4.6 mm) C18 reversed-phase column with guard column. All instruments and columns were obtained from Rainin. Solvent mixtures, as stated in the text, were obtained by mixing solvents degassed prior to use with helium. Flow rates between 0.8 and 1.0 mL/min were used. Preparative column: Dynamax Macro HPLC C18 column



**Figure 1.** Chromatograms of gold clusters for a 335/120/1 solvent, mixture of EtOH, H<sub>2</sub>O, and NH<sub>4</sub>NO<sub>3</sub> (w/w), at a flow rate of 0.70 mL/min: (a) mixture of Au<sub>6</sub>, Au<sub>8</sub>, Au<sub>9</sub>, and Au<sub>11</sub> clusters; (b) mixture of Au<sub>6</sub>, Au<sub>8</sub>, and Au<sub>9</sub> clusters.

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**Table I.** Chromatographic Data for Gold Cluster Compounds

compd	t <sub>R</sub> , min <sup>a</sup>	k'	N <sub>theor</sub>
[Au <sub>9</sub> (PPh <sub>3</sub> ) <sub>8</sub> ] <sup>3+</sup>	1.55	0.05	150
[Au <sub>6</sub> (PPh <sub>3</sub> ) <sub>6</sub> ] <sup>2+</sup>	2.09	0.41	350
[Au <sub>8</sub> (PPh <sub>3</sub> ) <sub>7</sub> ] <sup>2+</sup>	3.32	1.24	290
[Au <sub>8</sub> (PPh <sub>3</sub> ) <sub>8</sub> ] <sup>2+</sup>	4.76	2.22	160
[Au <sub>11</sub> (PPh <sub>3</sub> ) <sub>8</sub> (CNO) <sub>2</sub> ] <sup>+</sup>	8.51	4.75	255

<sup>a</sup> 20-μg samples with a 335/120/1 mixture of EtOH, H<sub>2</sub>O, and NH<sub>4</sub>NO<sub>3</sub> (w/w) at a flow rate of 0.70 mL/min.

(Rainin).

## Results and Discussion

**Gold Cluster Compounds.** When a cationic gold cluster compound such as [Au<sub>9</sub>(PPh<sub>3</sub>)<sub>8</sub>]<sup>3+</sup> is eluted on silica gel or alumina, it soon becomes immobilized regardless of the solvent used. If a small amount of HNO<sub>3</sub>, NH<sub>4</sub>NO<sub>3</sub>, NH<sub>4</sub>PF<sub>6</sub>, or CH<sub>3</sub>COOH is added to the solvent, however, the immobilized gold cluster starts to elute again. This effect can most satisfactorily be explained in terms of an ion-exchange process involving the gold clusters and the column material. The cationic gold clusters are accompanied by uncoordinated anions such as NO<sub>3</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, or BF<sub>4</sub><sup>-</sup>. During elution, the protons of the column material can be exchanged for gold clusters, resulting in the elution of the protonated counterions. The column material thus serves as a new immobile counterion. Addition of a proton source to the solvent continuously feeds the column material H<sup>+</sup> ions, which compete with the cationic gold clusters, resulting in elution of the latter. An ion-pairing mechanism is not likely to be operative, since the addition of a nonprotonated salt like [NBu<sub>4</sub>]NO<sub>3</sub> did not mobilize the gold cluster.

For the chromatography of gold clusters on regular silica gel TLC plates, 0.02 M NH<sub>4</sub>NO<sub>3</sub> in ethanol was used as an eluent. Gold clusters eluted well with this system, although some tailing was observed, sometimes leading to double zonation.<sup>34</sup> Despite good elution, separation of gold cluster compounds was not always possible, however. The retention times seemed to be dominated by the charge of the gold cluster cation. The 3+, 2+, and 1+ cluster cations showed R<sub>f</sub> values of 0.25, 0.45, and 0.55, respectively. Therefore, the R<sub>f</sub> values can feasibly be used as a predictive tool in charge determination.

By far the best results for the separation of gold cluster compounds have been obtained by using C18 reversed-phase silica gel

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Table II. Chromatographic Data for Mixed-Metal Cluster Compounds

compd	solvent mixture			flow, mL/min	$t_R$ , min	$N_{theor}$
	% H <sub>2</sub> O <sup>a</sup>	% EtOH	% CH <sub>3</sub> CN			
[AuRu( $\mu$ -H) <sub>2</sub> (dppm) <sub>2</sub> (PPh <sub>3</sub> ) <sup>+</sup> (two isomers)	25	60	15	1.0	10.21 12.43	800 800
[AuRu( $\mu$ -H) <sub>2</sub> (dppm) <sub>2</sub> (PPh <sub>3</sub> ) <sup>+</sup> (two isomers)	20 $\rightarrow$ 5 <sup>b</sup>	65 $\rightarrow$ 75	15 $\rightarrow$ 20	0.5	11.33 12.12	2000 2100
[Au <sub>2</sub> Ru( $\mu$ -H) <sub>2</sub> (dppm) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> <sup>2+</sup>	20 $\rightarrow$ 5 <sup>b</sup>	65 $\rightarrow$ 75	15 $\rightarrow$ 20	0.5	5.39	1100
{AuRu(H) <sub>2</sub> [P(OMe) <sub>3</sub> ] <sub>4</sub> (PPh <sub>3</sub> ) <sup>+</sup>	20 $\rightarrow$ 5 <sup>b</sup>	65 $\rightarrow$ 75	15 $\rightarrow$ 20	0.5	6.74	1300
[AuOs(H) <sub>2</sub> (CO) <sub>2</sub> (PPh <sub>3</sub> ) <sub>3</sub> <sup>+</sup>	10	70	20	0.5	5.98	2400
[AuOs(H) <sub>2</sub> (CO)(PPh <sub>3</sub> ) <sub>4</sub> <sup>+</sup>	10	70	20	0.5	6.96	1700
[AuOs <sub>2</sub> (H) <sub>3</sub> (PPh <sub>3</sub> ) <sub>5</sub> <sup>+</sup>	10	70	20	0.5	9.16	1300
[Au <sub>6</sub> Pt(PPh <sub>3</sub> ) <sub>7</sub> ] <sup>2+</sup>	20	60	20	0.5	10.06	1500
[Au <sub>7</sub> Pt(H)(PPh <sub>3</sub> ) <sub>8</sub> ] <sup>2+</sup>	20	60	20	0.5	17.06	900
[Au <sub>8</sub> Pt(PPh <sub>3</sub> ) <sub>8</sub> ] <sup>2+</sup>	20	60	20	0.5	14.75	1000
[Au <sub>4</sub> Re(H) <sub>4</sub> [P( <i>p</i> -tol) <sub>3</sub> ] <sub>2</sub> (PPh <sub>3</sub> ) <sub>4</sub> ] <sup>+</sup>	15	60	25	0.5	6.28	1200
[Au <sub>3</sub> Re(H) <sub>4</sub> [P( <i>p</i> -tol) <sub>3</sub> ] <sub>2</sub> (PPh <sub>3</sub> ) <sub>5</sub> ] <sup>2+</sup>	15	60	25	0.5	9.14	900

<sup>a</sup>0.125 M NH<sub>4</sub>PF<sub>6</sub> solution in water. <sup>b</sup>Linear gradient over 15 min.

eluted with a 335/120/1 mixture of ethanol, water, and NH<sub>4</sub>NO<sub>3</sub> (w/w). Because of the hydrophobic character of the column, the elution order was reversed compared to that of polar columns, with highly charged gold clusters such as [Au<sub>9</sub>(PPh<sub>3</sub>)<sub>8</sub>]<sup>3+</sup> eluting first. With this type of column material, addition of NH<sub>4</sub>NO<sub>3</sub>, NH<sub>4</sub>PF<sub>6</sub>, or NaBF<sub>4</sub> was still necessary for the elution of cationic gold cluster compounds. There was no observable difference in separation when any of these salts were used. The fact that the nonprotonic NaBF<sub>4</sub> could be used here suggests that, in contrast to elution on silica gel, an ion pairing mechanism cannot be ruled out completely. The separation was influenced by the amount of salt added. Too little salt resulted in very slow elution and heavy tailing, whereas too much salt resulted in fast elution and poor separations.

Separations of gold clusters were carried out by using a new type of glass cartridge column (dimensions 100  $\times$  3 mm). Glass cartridges have the advantage of being transparent, which is especially useful in checking for metal contamination of the column. They are also inexpensive, are easy to replace, and serve solvent economy, without the special need for microbore equipment. The gold cluster compounds were monitored by UV detection at 254 nm.

Figure 1 shows two typical chromatograms of mixtures of the gold clusters [Au<sub>9</sub>(PPh<sub>3</sub>)<sub>8</sub>]<sup>3+</sup>, [Au<sub>6</sub>(PPh<sub>3</sub>)<sub>6</sub>]<sup>2+</sup>, [Au<sub>8</sub>(PPh<sub>3</sub>)<sub>7</sub>]<sup>2+</sup>, [Au<sub>8</sub>(PPh<sub>3</sub>)<sub>8</sub>]<sup>2+</sup>, and [Au<sub>11</sub>(PPh<sub>3</sub>)<sub>8</sub>(CNO)<sub>2</sub>]<sup>+</sup>. All of the gold cluster compounds were separated completely except for [Au<sub>9</sub>(PPh<sub>3</sub>)<sub>8</sub>]<sup>3+</sup> and [Au<sub>6</sub>(PPh<sub>3</sub>)<sub>6</sub>]<sup>2+</sup>. By use of a preparative column of sufficient length, however, these two compounds could be separated completely as well. The peaks in Figure 1 show some tailing (asymmetry factors between 1.3 and 1.7), indicating increasing retention times with decreasing concentrations. Separate experiments showed a decrease in retention time ranging from 7 to 17% when the sample amount was increased from 10 to 200  $\mu$ g. For general analytical purposes this did not lead to identification problems.

In Table I the retention times ( $t_R$ ), capacity factors  $k'$  (calculated from  $k' = (t_R - t_M)/t_M$ , where  $t_M$  is the retention time of the mobile phase), and theoretical plate numbers (calculated from  $N_{theor} = 5.54[t_R/(w_{1/2})]^2$ , where  $w_{1/2}$  is the peak width at half-height) are listed for these gold clusters. The plate numbers are relatively low, as a result of the broad peaks produced by the gold clusters. Non-gold cluster compounds, like ferrocene, produced plate numbers of ca. 1000 on the same column. The broad peaks might be a result of equilibria reactions in which the gold clusters are involved. Therefore, it is somewhat surprising that the separations are as good as they are. The periphery of the gold cluster ions is covered by the many phenyl groups of the PPh<sub>3</sub> ligands. It therefore seems likely that they dominate the interaction of the gold clusters with the column material. We also know that the charge is important, since more highly charged gold clusters are retained less than lower charged clusters. In looking at the equally charged gold clusters [Au<sub>6</sub>(PPh<sub>3</sub>)<sub>6</sub>]<sup>2+</sup>, [Au<sub>8</sub>(PPh<sub>3</sub>)<sub>7</sub>]<sup>2+</sup>, and [Au<sub>8</sub>(PPh<sub>3</sub>)<sub>8</sub>]<sup>2+</sup>, however, we observe that there

is an increase in retention time with increasing number of phosphines.

**Mixed-Metal Cluster Compounds.** In addition to the separation of gold cluster compounds, a variety of mixed-metal cluster compounds containing gold were examined. The separations were conducted on a regular C18 silica gel column (250  $\times$  4.6 mm) by using solvent mixtures similar to those used for the separation of gold clusters. Sometimes the addition of up to 20% acetonitrile was used to improve the resolution of the peaks. CH<sub>3</sub>CN also helped to increase the solubility of the compounds in the eluent. UV detection at 254 nm was used, as all compounds contained aromatic groups. Peak symmetry and broadness were in general much better for mixed-metal clusters than for gold clusters. Parameters are listed in Table II.

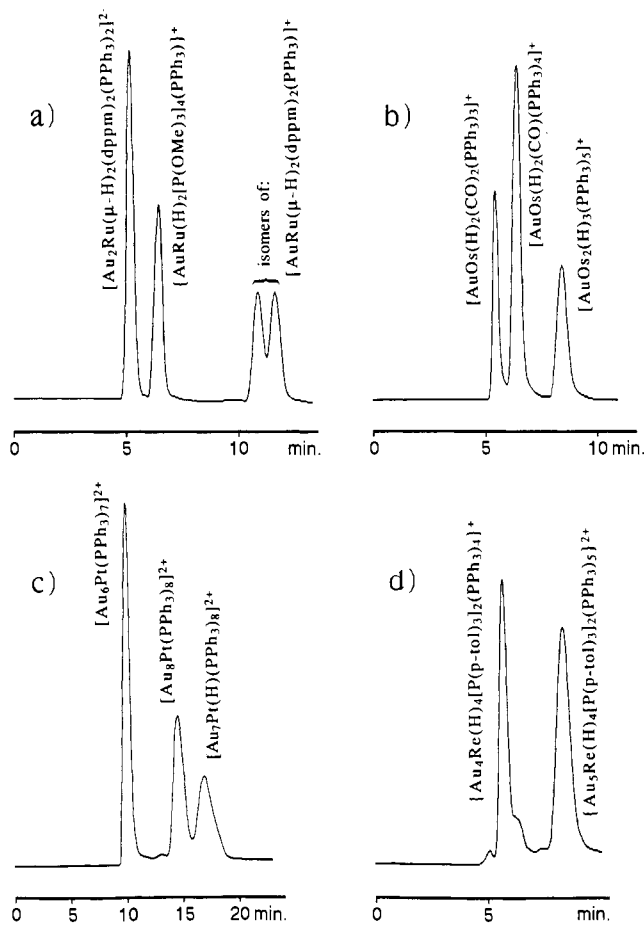
[AuRu( $\mu$ -H)<sub>2</sub>(dppm)<sub>2</sub>(PPh<sub>3</sub>)<sup>+</sup> consists of two isomers that are in equilibrium in solution.<sup>21</sup> These two isomers were separated with use of a solvent mixture of 25% 0.125 M NH<sub>4</sub>PF<sub>6</sub>, 60% EtOH, and 15% CH<sub>3</sub>CN, with a resolution of 1.3 (calculated from  $R = (t_{R2} - t_{R1})/[0.5(w_1 + w_2)]$ ). With gradient elution, in which the eluent was gradually changed over 15 min from 20% 0.125 M NH<sub>4</sub>PF<sub>6</sub>, 65% EtOH, and 15% CH<sub>3</sub>CN to 5% 0.125 M NH<sub>4</sub>PF<sub>6</sub>, 75% EtOH, and 20% CH<sub>3</sub>CN, the resolution of these two isomer peaks was reduced to 0.8. These conditions, however, provided a good separation of a mixture of the Ru-Au clusters [AuRu( $\mu$ -H)<sub>2</sub>(dppm)<sub>2</sub>(PPh<sub>3</sub>)<sup>+</sup>, [Au<sub>2</sub>Ru( $\mu$ -H)<sub>2</sub>(dppm)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub><sup>2+</sup>, and [AuRu(H)<sub>2</sub>[P(OMe)<sub>3</sub>]<sub>4</sub>(PPh<sub>3</sub>)<sup>+</sup> (see Figure 2a). As expected with this type of column, the lower charged clusters were retained longer than the more highly charged compounds. With the equally charged species [AuRu( $\mu$ -H)<sub>2</sub>(dppm)<sub>2</sub>(PPh<sub>3</sub>)<sup>+</sup> and {AuRu(H)<sub>2</sub>[P(OMe)<sub>3</sub>]<sub>4</sub>(PPh<sub>3</sub>)<sup>+</sup>, the latter complex was eluted first, due to the more polar character of the P(OMe)<sub>3</sub> ligands.

The separation of the gold-osmium clusters [AuOs(H)<sub>2</sub>(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>]<sup>+</sup>, [AuOs(H)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>4</sub>]<sup>+</sup>, and [AuOs<sub>2</sub>(H)<sub>3</sub>(PPh<sub>3</sub>)<sub>5</sub>]<sup>+</sup> is shown in Figure 2b. They were separated by using a mixture of 10% 0.125 M NH<sub>4</sub>PF<sub>6</sub>, 70% EtOH, and 20% CH<sub>3</sub>CN, with resolutions of 1.6 and 2.5, respectively. Analogous to what was observed with gold clusters, the retention of the osmium-gold clusters increased as the number of triphenylphosphines in the cluster increased, due to decreasing polarity.

The platinum-gold clusters [Au<sub>6</sub>Pt(PPh<sub>3</sub>)<sub>7</sub>]<sup>2+</sup>, [Au<sub>7</sub>Pt(H)(PPh<sub>3</sub>)<sub>8</sub>]<sup>2+</sup>, and [Au<sub>8</sub>Pt(PPh<sub>3</sub>)<sub>8</sub>]<sup>2+</sup> showed a similar elution behavior when separated with a mixture of 20% 0.125 M NH<sub>4</sub>PF<sub>6</sub>, 60% EtOH, and 20% CH<sub>3</sub>CN (see Figure 2c).

Finally, two rhenium-gold clusters, [Au<sub>4</sub>Re(H)<sub>4</sub>[P(*p*-tol)<sub>3</sub>]<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>]<sup>+</sup>, and [Au<sub>3</sub>Re(H)<sub>4</sub>[P(*p*-tol)<sub>3</sub>]<sub>2</sub>(PPh<sub>3</sub>)<sub>5</sub>]<sup>2+</sup> were separated by using a mixture of 15% 0.125 M NH<sub>4</sub>PF<sub>6</sub>, 60% EtOH, and 25% CH<sub>3</sub>CN as shown in Figure 2d.

The same solvent conditions that were used for the analytical separation of the metal cluster compounds stated above could also be used to separate the compounds on a larger scale with use of a preparative column with the same column material. A preparative-scale separation is useful when complex reactions mixtures of metal clusters cannot be purified in any other way. Also, it



**Figure 2.** Chromatograms of mixed-metal-gold clusters run at a flow rate of 0.5 mL/min with the following solvent conditions: (a) linear gradient changing from 20% 0.125 M  $\text{NH}_4\text{PF}_6$ , 65% EtOH, and 15%  $\text{CH}_3\text{CN}$  to 5% 0.125 M  $\text{NH}_4\text{PF}_6$ , 75% EtOH, and 20%  $\text{CH}_3\text{CN}$  in 15 min; (b) 10% 0.125 M  $\text{NH}_4\text{PF}_6$ , 70% EtOH, and 20%  $\text{CH}_3\text{CN}$ ; (c) 20% 0.125 M  $\text{NH}_4\text{PF}_6$ , 60% EtOH, and 20%  $\text{CH}_3\text{CN}$ ; (d) 15% 0.125 M  $\text{NH}_4\text{PF}_6$ , 60% EtOH, and 25%  $\text{CH}_3\text{CN}$ .

is often much easier to grow crystals of a cluster after purification by preparative-scale HPLC.

### Conclusion

Reversed-phase HPLC chromatography on silica gel C18 has proven to be a useful technique for the separation and identification of cationic gold and a variety of mixed-metal-gold cluster compounds. Only minor changes in solvent composition have been necessary for the successful separation of these different mixed-metal clusters. HPLC has also been shown to be a fast and very sensitive technique for the detection of reactions and identification of compounds, and preparative HPLC is a convenient way of separating different reaction products.

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**Registry No.**  $[\text{Au}_9(\text{PPh}_3)_8]^{3+}$ , 60477-23-8;  $[\text{Au}_6(\text{PPh}_3)_6]^{2+}$ , 60477-20-5;  $[\text{Au}_8(\text{PPh}_3)_8]^{2+}$ , 74245-04-8;  $[\text{Au}_8(\text{PPh}_3)_8]^{2+}$ , 72187-44-1;  $[\text{Au}_{11}(\text{PPh}_3)_8(\text{CNO})_2]^{2+}$ , 98921-32-5;  $[\text{AuRu}(\mu\text{-H})_2(\text{dppm})_2(\text{PPh}_3)]^+$ , 108969-21-7;  $[\text{Au}_2\text{Ru}(\mu\text{-H})_2(\text{dppm})_2(\text{PPh}_3)_2]^{2+}$ , 102538-83-0;  $[\text{AuRu}(\text{H})_2[\text{P}(\text{OMe})_3]_4(\text{PPh}_3)]^+$ , 108969-25-1;  $[\text{AuOs}(\text{H})_2(\text{CO})_2(\text{PPh}_3)_3]^+$ , 112681-80-8;  $[\text{AuOs}(\text{H})_2(\text{CO})(\text{PPh}_3)_4]^+$ , 112681-81-9;  $[\text{AuOs}_2(\text{H})_3(\text{PPh}_3)_5]^{2+}$ , 112681-82-0;  $[\text{Au}_6\text{Pt}(\text{PPh}_3)_7]^{2+}$ , 107712-38-9;  $[\text{Au}_7\text{Pt}(\text{H})(\text{PPh}_3)_8]^{2+}$ , 110870-02-5;  $[\text{Au}_8\text{Pt}(\text{PPh}_3)_8]^{2+}$ , 110870-04-7;  $[\text{Au}_4\text{Re}(\text{H})_4[\text{P}(p\text{-tol})_3]_2(\text{PPh}_3)_4]$ , 107712-40-3;  $[\text{Au}_5\text{Re}(\text{H})_4[\text{P}(p\text{-tol})_3]_2(\text{PPh}_3)_5]$ , 107742-33-6.

Contribution from the Department of Chemistry, University of Florence, Via G. Capponi 7, 50121 Florence, Italy, IBM T. J. Watson Research Center, Yorktown Heights, New York 10598, and Institute of Agricultural Chemistry, Faculty of Agricultural Sciences, University of Bologna, Bologna, Italy

### Electronic Relaxation of a Copper(II) Dimer in a Macromolecular Complex As Evaluated from Solvent Proton Relaxation

Ivano Bertini,<sup>\*1a</sup> Lucia Banci,<sup>1a</sup> Rodney D. Brown III,<sup>1b</sup> Seymour H. Koenig,<sup>1b</sup> and Claudio Luchinat<sup>1a,c</sup>

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Bovine erythrocyte superoxide dismutase (SOD) is a dimeric enzyme containing one copper and one zinc per monomeric subunit.<sup>2</sup> The structure of the copper-zinc region, as found by X-ray crystallography, is shown in Figure 1. The protein can be readily demetallated, and a variety of metal-substituted forms have been described.<sup>3</sup> The  $\text{Cu}^{2+}$  ions within each monomer of dimeric  $\text{Cu}_2\text{Cu}_2\text{SOD}$  are antiferromagnetically coupled, with  $2J = -52 \text{ cm}^{-1}$  and an  $S = 0$  ground state. However, they have an EPR spectrum typical of an  $S = 1$  system,<sup>4</sup> arising from population of the excited states. We have now investigated the apoSOD/ $\text{Cu}^{2+}$  system by measuring the longitudinal magnetic relaxation rate  $1/T_1$  of water protons in solutions containing apoSOD plus increasing amounts of  $\text{Cu}^{2+}$ , at field values ranging from 0.23 mT to 1.17 T (0.01–50 MHz proton Larmor frequency), and at 25 °C, which corresponds to  $kT \gg J$ . The variation of  $1/T_1$  with field is known as the nuclear magnetic relaxation dispersion (NMRD) profile.<sup>5-7</sup> The theory is now available to interpret NMRD profiles of  $\text{Cu}^{2+}$  systems<sup>6,7</sup> by using as adjustable parameters (1)  $r_{\text{Cu-H}}$ , the  $\text{Cu}^{2+}$ -proton separation of the inner-coordinated waters, (2)  $\theta$ , the average angle of the metal-proton vector with respect to the  $z$  axis of the electron-copper nucleus hyperfine coupling tensor (assumed to be axial), and (3) the correlation time of the  $\text{Cu}^{2+}$ -proton magnetic dipolar interaction (assumed to be field independent), which is dominated by the electronic relaxation time  $\tau_S$  in  $\text{Cu}^{2+}$ -protein systems.<sup>6</sup> The present aim is to measure the correlation time of magnetically coupled  $\text{Cu}^{2+}$  systems and—by equating it to  $\tau_S$ —evaluate the extension of the now well-established theory to the more complex case of magnetically coupled systems.<sup>6,8</sup> These points are key for understanding the electronic structure of coupled dimers of paramagnetic ions, in a general sense. In addition, NMRD profiles are very sensitive to the uptake of copper ions by apoSOD, allowing one to obtain protein-specific biochemical information on the sequential binding of  $\text{Cu}^{2+}$  to the copper and zinc sites of the native enzyme and on the respective binding affinities.

### Materials and Methods

Native SOD was purchased from Diagnostic Data Inc., Mountain View, CA. Apoprotein was prepared as previously reported,<sup>10,11</sup> recon-

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