

The slope of this plot,  $1.26 \pm 0.05$ , indicates that the nucleophilic discrimination power of the dimethyl sulfoxide complex is some 26% greater than that of the ammonia complex. A relationship between cis effect and the nucleophilic discrimination factor of the substrate indicates that we must look to the bond-forming transition state for the main site of the effect. The greater nucleophilic discrimination of the dimethyl sulfoxide complex suggests that it is better able to counteract the effects of the extra electron density brought in by the entering nucleophile than the ammonia complex.

Also included in Table III are rate constants for the replacement of  $\text{Cl}^-$  from  $[\text{Pt}(\text{dien})\text{Cl}]^+$  (dien = 1,5-diamino-3-azapentane) which have been extrapolated to  $\mu = 0$ , by using the expression discussed above, and to 25 °C, by using published activation parameters. It is of interest to note that, while the solvolytic rate constant is similar in magnitude to those of the other two complexes, the values of  $k_2^\circ$  are somewhat larger than the corresponding values for the  $[\text{Pt}(\text{en})(\text{NH}_3)\text{Cl}]^+$  cation. A log-log plot comparing these two sets of data is shown in Figure 2 and suggests that the difference in behavior is due to a small (slope =  $1.038 \pm 0.020$ ) but significant difference in the nucleophilic discrimination factors of the two substrates. It has been shown that the cis effect of an amine is quite significant and depends upon its proton basicity, the least basic amine generating the most labile substrate.<sup>6</sup> If one assumes that the ethylenediamine ring and one of the dien rings were equivalent and that ammonia had a stronger cis effect than the more basic  $-\text{CH}_2\text{NH}_2$ , then one would predict that  $[\text{Pt}(\text{dien})\text{Cl}]^+$  should be less reactive than  $[\text{Pt}(\text{en})(\text{NH}_3)\text{Cl}]^+$ . The contrary observation indicates that the problem is more complicated. It might be argued that coordination of the other nitrogens in dien might greatly decrease the basicity of the third, but the relative importance of transmitting these effects through the aliphatic chains and through the platinum has been discussed elsewhere<sup>9</sup> and it was concluded that the linking of the nitrogens by aliphatic chains was only of secondary importance.

The greater cis effect of the sulfur in dimethyl sulfoxide compared to that of nitrogen in ammonia cannot be ascribed to the weaker  $\sigma$  donation that was invoked to account for the

variation of the amine cis effect.<sup>6</sup> There is strong evidence to suggest that, in the ground state at least, sulfur is the better donor. However, the greater polarizability of the sulfur may allow some transfer of charge away from the reaction center through the  $\sigma$  framework as the incoming group becomes bound. Although we cannot rule out the possibility of charge withdrawal through the  $\pi$ -acceptor properties of sulfur, it should be realized that in these cationic complexes, the nonbonding d electrons on the metal are not readily available for such interaction. The most important thing to realize is that the magnitude of the "electronic" cis effect is small and the meaningfulness of any naive attempt to characterize these electron displacements in terms of polarizations, polarizabilities, or  $\sigma$  or  $\pi$  effects is equally small.

Mention should be made in passing of the departures from the reactivity order predicted by the  $n_{\text{Pt}}^\circ$  values assigned to the nucleophiles. The potentially biphilic reagents are less reactive than predicted because the substrate is cationic and the relevant nonbonding electrons on the metal are less available for bonding with the entering group. It is less clear why thiocyanate should be less reactive than expected toward  $\text{Me}_2\text{SO}$  complex, becoming less reactive than iodide, and why azide becomes more reactive than bromide toward the ammonia complex but not toward the dien or the  $\text{Me}_2\text{SO}$  complex. These effects are small but, nevertheless, significant. It is possible that they are a minor manifestation of the well-known "steric hindrance" cis effect but much remains to be done before this aspect of the problem can be adequately discussed.

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**Supplementary Material Available:** A listing of  $k_{\text{obsd}}$  as a function of  $[\text{X}^-]$  and ionic strength (5 pages). Ordering information is given on any current masthead page.

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## Crystal Structure of Ammonium Dicobalto(II)-40-tungstotetraarsenate(III). Allosteric Effects in the Ligand

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Crystals of  $(\text{NH}_4)_{23}(\text{NH}_4\text{As}_4\text{W}_{40}\text{O}_{140}\text{Co}_2(\text{H}_2\text{O})_2) \cdot n\text{H}_2\text{O}$  ( $18 \leq n \leq 20$ ) are orthorhombic, of space group  $Pm\bar{m}n$ , with  $a = 29.688$  (7) Å,  $b = 23.327$  (6) Å,  $c = 12.794$  (3) Å, and  $Z = 2$ . The structure was determined from 3989 reflections collected on an automatic diffractometer and refined by a full-matrix least-squares method to  $R = 0.065$ . The ligand shows two types of coordination sites: an  $\text{NH}_4^+$  ion is in a central site (S1) and two  $\text{NH}_4^+$  and two  $\text{Co}^{2+}$  are in external coordination sites (S2). Interactions between these sites, depending on their relative positions, are discussed. In this complex the ligand is a cyclic system consisting of four  $\text{AsW}_9\text{O}_{33}$  subunits related through a pseudo  $\bar{4}$  axis and joined up by four extra  $\text{WO}_6$  octahedra.

The formation of polynuclear complexes between tungsten and arsenic or antimony at the oxidation state III has been previously reported.<sup>1-3</sup> We recently developed this study for

two reasons: (a)  $\text{As}^{\text{III}}$  and  $\text{Sb}^{\text{III}}$  have a stereochemically active lone pair of electrons which is involved in the formation of the polyanionic structures; (b) these complexes show antiviral and antitumoral activities at noncytotoxic doses "in vitro"<sup>4-6</sup> and

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"in vivo"<sup>7,8</sup> and are powerful inhibitors of cellular, bacterial, and viral DNA and RNA polymerases.<sup>9</sup> Structural studies were necessary to understand the relationships between the structure and the chemical or biological properties. A first structure was determined by Fisher et al. of the tungsto-antimonate ( $\text{NaSb}_9\text{W}_{21}\text{O}_{86}$ )<sup>18-20</sup>

With arsenic, the formation and the physicochemical properties of the ligand ( $\text{As}_4\text{W}_{40}\text{O}_{140}$ )<sup>28-</sup> (hereafter noted L) have been reported.<sup>2</sup> The main features are (1) L reacts with alkaline and alkaline-earth ions (noted  $\text{M}^{n+}$ ), leading to cryptates  $\text{ML}$ , with the highest affinity for  $\text{K}^+$  and  $\text{Ba}^{2+}$ ; (2)  $\text{ML}$  reacts with transition-metal ions (noted  $\text{Z}^{n+}$ ), leading to  $\text{MLZ}_2$  complexes, and (3)  $\text{ML}$  reacts with  $\text{Ag}^+$ , leading to  $\text{MLAg}_4$  complexes;  $\text{MLZ}_2\text{Ag}_2$  complexes can be obtained by either action of  $\text{Ag}^+$  on  $\text{MLZ}_2$  or substituting  $\text{Ag}$  with  $\text{Z}$  on  $\text{MLAg}_4$ .

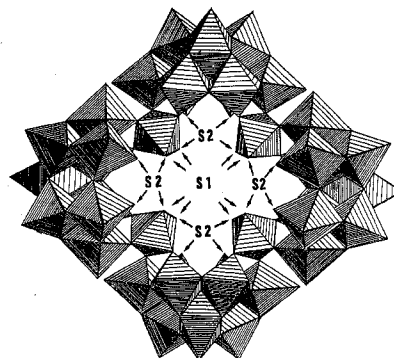
Several questions arise from these results. In particular, what is the basis of the selectivity for  $\text{K}^+$  and  $\text{Ba}^{2+}$ ? Why do only two  $\text{Z}^{n+}$  transition-metal ions but four  $\text{Ag}^+$  ions react with  $\text{ML}$ ? So, an X-ray investigation appeared necessary to establish the whole geometry of the ligand and its structural relationships with the complexed metals.

## Experimental Section

**Preparation of the Compound.** The crystallographic study has been carried out on  $(\text{NH}_4)_{23}(\text{NH}_4\text{As}_4\text{W}_{40}\text{O}_{140}(\text{CoH}_2\text{O})_2) \cdot n\text{H}_2\text{O}$  with  $18 \leq n \leq 20$ .

A molar solution of  $\text{Co}(\text{NO}_3)_2$  (10 mL) was added to a solution of the sodium salt of the ligand prepared as previously described<sup>2</sup> (60 g in 300 mL of water). The ammonium salt of the complex was precipitated by addition of solid ammonium nitrate (30 g). After filtration, the precipitate was twice dissolved and precipitated again by ammonium nitrate in order to obtain a sodium free salt. The latter was crystallized from aqueous solution at  $\text{pH} \geq 6$ . The crystals were shaped as thin green needles.

**X-ray Diffraction.** The unit cell dimensions and space group were preliminarily determined from oscillation and Weissenberg photographs. The symmetry was orthorhombic and the systematic absences ( $hk0$  with  $h + k \neq 0$ ) led either to centrosymmetric  $Pm\bar{m}n$  or to noncentrosymmetric  $Pmn_21$  space groups. Statistics on normalized structure factors  $E_{hkl}$  led unambiguously to the centrosymmetric  $Pm\bar{m}n$  group. Thereafter the second setting of ref 11 (origin at  $\bar{1}$ ) has been used. The measured density agreed with the calculated one ( $d_{\text{calcd}} = 4.10$ ,  $d_{\text{measd}} = 4.05$ ) for  $Z = 2$ . This implies that the asymmetric unit is only one-fourth of the polyanion. A  $0.30 \times 0.17 \times 0.07$  mm<sup>3</sup> parallelepiped crystal was set with its "c" axis along the  $\phi$  axis of a CAD-3 Enraf-Nonius diffractometer. A least-squares fit to the setting of 24 independent reflections led to the cell parameters  $a = 29.688$  (7),  $b = 23.327$  (6), and  $c = 12.794$  (3) Å. Intensities were collected at room temperature in the  $\theta$ - $2\theta$  scan mode with  $\text{Mo K}\alpha$  radiation ( $\lambda_{\text{MoK}\alpha} = 0.71069$  Å) Zr filtered up to  $(\sin \theta)/\lambda = 0.4822$ . A standard deviation based on counting statistics was assigned to each reflection. A total of 3989 independent reflections of one octant were collected; among them 2343 with  $I > 1.5\sigma(I)$  were considered as observed. Their intensities were corrected for the Lorentz and polarization factors. Absorption corrections were necessary ( $\mu = 284$



**Figure 1.** Polyhedral model of the ligand  $\text{As}_4\text{W}_{40}\text{O}_{140}^{28-}$  structure in the complex. Octahedra outline the octahedral tungsten coordination polyhedra. Arsenic atoms are omitted for clarity. Arrows indicate the coordinative oxygen atoms of the central site S1 and of the four coordination sites S2.

$\text{cm}^{-1}$ ). They were carried out with a local version of ORABS.<sup>12</sup> The highest and lowest values of the transmission coefficient were respectively 0.136 and 0.013. A Wilson plot gave the scale and the overall temperature factor ( $B = 1.84$  Å<sup>2</sup>).

**Solution of the Structure.** The structure was solved by direct methods. Normalized structure factors  $E_{hkl}$  were computed and introduced in a MULTAN procedure.<sup>13</sup> A total of 400 reflections with  $E_{hkl} > 1.96$  were used to determine the starting sets. As it was not possible to interpret the  $E$  map in chemical terms, the most probable starting set was assumed to be the right one. The 11 highest peaks were introduced as tungsten atoms in a least-squares refinement which gave an  $R$  factor of 0.23. Alternate Fourier syntheses and least-squares refinements showed up all the other atoms of the polyanion. Then the  $R$  factor was 0.15. The anisotropic treatment of the thermal parameters of W, As, and Co atoms led to  $R = 0.10$ . The 17 remaining peaks (ammonium ions and water molecules) were introduced as oxygen atoms and refined to an  $R$  factor of 0.078. The  $B$  values for these atoms appeared divided in two groups, the first one ranging from 0 to 5 Å<sup>2</sup> and the second from 5 to 12 Å<sup>2</sup>. In the last least-squares cycles an attempt to differentiate the ammonium ions from the water molecules was to assume that the ammonium ions had the greatest temperature factors when introduced as oxygen atoms. The introduction of the scattering factors of nitrogen for these atoms reduced the  $B$  value scattering (0 to 6), and the  $R$  factor dropped to 0.075. However these assignments remained doubtful because the electron densities of the ammonium ions and water molecules are too close and too weak with respect to tungsten atoms. Moreover, for the same reason, while thermogravimetric determinations led to a number of hydration molecules  $18 \leq n \leq 20$ , only 16 molecules of water were found by X-ray diffraction. In the last least-squares cycles a weighted scheme of the form  $w = (1055 - 7F_o)^{-1}$  for  $F_o < 150$  and  $w = (6 + 1.08F_o)^{-1}$  for  $F_o > 150$  was applied. The final  $R$  values are  $R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.065$  and  $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w F_o^2)^{1/2} = 0.077$ . In the last refinement cycle, the ratios of largest shift to standard deviation in coordinates were smaller than  $10^{-3}$  for W, As, and Co atoms and smaller than  $2 \times 10^{-3}$  for other atoms. The final coordinates and the symmetry code are listed in Table I.

All calculations were carried out on an IBM 370-168 computer with local versions of ORFLS<sup>14</sup> for least-squares calculations, GEST<sup>15</sup> for Fourier syntheses, and NRC programs<sup>16</sup> for geometrical calculations. The scattering factors were taken from ref 11 for neutral atoms. Real

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Table I. Atomic Coordinates and Thermal Parameters<sup>a</sup>

atom	$x/a$	$y/b$	$z/c$	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$	$B_{\text{eqv}}, \text{\AA}^2$
W(1)	0.750 00	0.388 05 (17)	0.278 07 (33)	0.000 62 (5)	0.000 64 (8)	0.004 21 (33)	0	0	0.000 37 (14)	2.11 (19)
W(2)	0.692 28 (9)	0.505 07 (12)	0.353 54 (22)	0.000 50 (3)	0.000 86 (6)	0.003 44 (20)	-0.000 01 (4)	0.000 09 (7)	0.000 18 (9)	1.96 (12)
W(3)	0.687 09 (10)	0.389 10 (12)	0.027 50 (23)	0.000 75 (4)	0.000 64 (5)	0.004 16 (22)	-0.000 17 (4)	-0.000 34 (8)	-0.000 22 (10)	2.25 (13)
W(4)	0.628 78 (9)	0.507 04 (12)	0.105 04 (23)	0.000 52 (3)	0.000 87 (6)	0.004 17 (21)	-0.000 11 (4)	-0.000 15 (7)	-0.000 08 (10)	2.15 (12)
W(5)	0.688 60 (10)	0.510 34 (13)	-0.119 77 (24)	0.000 86 (4)	0.001 17 (6)	0.003 47 (21)	-0.000 13 (4)	-0.000 29 (8)	0.000 08 (10)	2.62 (13)
W(6)	0.453 85 (14)	0.750 00	0.199 92 (33)	0.000 41 (5)	0.001 28 (9)	0.003 39 (29)	0	-0.000 01 (11)	0	2.15 (19)
W(7)	0.547 01 (10)	0.677 06 (12)	0.125 42 (22)	0.000 56 (3)	0.001 00 (5)	0.003 14 (19)	-0.000 03 (4)	-0.000 17 (7)	-0.000 25 (10)	2.07 (11)
W(8)	0.456 20 (10)	0.669 80 (13)	0.451 37 (23)	0.000 50 (3)	0.001 28 (6)	0.004 11 (21)	-0.000 15 (4)	0.000 20 (8)	0.000 14 (11)	2.41 (12)
W(9)	0.547 06 (10)	0.591 39 (11)	0.365 63 (24)	0.000 65 (4)	0.000 91 (5)	0.004 29 (23)	-0.000 09 (4)	0.000 06 (8)	0.000 30 (10)	2.36 (13)
W(10)	0.554 26 (10)	0.671 60 (14)	0.586 33 (30)	0.000 68 (4)	0.001 48 (7)	0.003 52 (20)	-0.000 09 (5)	0.000 02 (8)	0.000 46 (11)	2.64 (14)
W(11)	0.658 10 (9)	0.643 35 (12)	0.245 23 (24)	0.000 48 (3)	0.000 78 (5)	0.003 52 (19)	-0.000 09 (4)	0.000 03 (8)	0.000 05 (10)	1.90 (11)
As(1)	0.750 0	0.526 2 (4)	0.113 0 (8)	0.000 6 (1)	0.000 8 (2)	0.002 6 (7)	0	0	0.000 3 (3)	1.9 (4)
As(2)	0.561 3 (3)	0.750 0	0.360 8 (8)	0.000 5 (1)	0.001 0 (2)	0.003 0 (7)	0	-0.000 2 (3)	0	2.0 (4)
Co	0.641 6 (4)	0.750 0	0.450 6 (11)	0.000 5 (2)	0.000 8 (3)	0.004 7 (11)	0	-0.000 8 (3)	0	2.2 (5)
atom	$x/a$	$y/b$	$z/c$	$B, \text{\AA}^2$	atom	$x/a$	$y/b$	$z/c$	$B, \text{\AA}^2$	
O <sub>a</sub> (1,2,2II) <sup>b</sup>	0.750	0.491 (3)	0.235 (6)	3.7 (16)	O <sub>a</sub> (6,7,7III)	0.529 (2)	0.750	0.256 (5)	1.5 (12)	
O <sub>a</sub> (3,4,5)	0.704 (1)	0.487 (2)	0.058 (3)	1.9 (9)	O <sub>a</sub> (8,9,10)	0.534 (1)	0.691 (1)	0.420 (3)	0.4 (7)	
O <sub>b</sub> (1,3)	0.706 (2)	0.122 (2)	0.176 (4)	3.7 (11)	O <sub>b</sub> (6,8)	0.450 (2)	0.693 (2)	0.309 (4)	3.0 (10)	
O <sub>b</sub> (2,4)	0.654 (2)	0.487 (2)	0.244 (5)	4.8 (13)	O <sub>b</sub> (7,9)	0.530 (2)	0.622 (3)	0.230 (4)	2.6 (10)	
O <sub>b</sub> (2,11)	0.693 (1)	0.583 (1)	0.296 (3)	0.5 (7)	O <sub>b</sub> (7,11)	0.606 (1)	0.679 (2)	0.188 (3)	1.6 (8)	
O <sub>b</sub> (4,11)	0.646 (1)	0.580 (2)	0.142 (3)	1.5 (8)	O <sub>b</sub> (9,11)	0.606 (1)	0.610 (2)	0.336 (4)	2.3 (9)	
O <sub>b</sub> (3,3II)	0.250	0.628 (3)	-0.004 (5)	2.6 (15)	O <sub>b</sub> (8,8III)	0.448 (2)	0.750	0.493 (5)	2.0 (13)	
O <sub>b</sub> (5,5II)	0.750	0.484 (2)	-0.153 (5)	1.7 (12)	O <sub>b</sub> (10,10III)	0.530 (2)	0.750	0.605 (6)	3.7 (16)	
O <sub>c</sub> (1,2)	0.708 (2)	0.073 (2)	0.366 (4)	2.9 (10)	O <sub>c</sub> (7,7III)	0.560 (2)	0.750	0.061 (4)	0.7 (11)	
O <sub>c</sub> (2,2II)	0.750	0.526 (2)	0.421 (4)	1.0 (11)	O <sub>c</sub> (8,9)	0.482 (1)	0.607 (2)	0.407 (4)	2.3 (9)	
O <sub>c</sub> (3,4)	0.634 (1)	0.421 (2)	0.078 (4)	2.3 (9)	O <sub>c</sub> (9,10)	0.558 (2)	0.599 (2)	0.503 (4)	2.8 (10)	
O <sub>c</sub> (4,5)	0.629 (2)	0.517 (2)	-0.040 (4)	2.8 (10)	O <sub>c</sub> (3,5)	0.676 (1)	0.423 (2)	-0.103 (3)	1.4 (9)	
O <sub>c</sub> (6,7)	0.481 (1)	0.702 (2)	0.113 (4)	2.2 (9)	O <sub>c</sub> (8,10)	0.487 (2)	0.661 (3)	0.576 (5)	5.5 (16)	
O <sub>d</sub> (1)	0.750	0.317 (3)	0.332 (5)	2.2 (13)	O <sub>d</sub> (6)	0.406 (2)	0.750	0.151 (5)	2.3 (13)	
O <sub>d</sub> (2)	0.659 (1)	0.511 (2)	0.463 (3)	1.3 (8)	O <sub>d</sub> (7)	0.552 (2)	0.634 (2)	0.020 (4)	3.6 (11)	
O <sub>d</sub> (3)	0.665 (2)	0.179 (2)	0.008 (4)	3.5 (11)	O <sub>d</sub> (8)	0.402 (1)	0.642 (2)	0.490 (3)	0.9 (7)	
O <sub>d</sub> (4)	0.575 (2)	0.507 (2)	0.131 (4)	4.2 (12)	O <sub>d</sub> (9)	0.541 (2)	0.522 (3)	0.338 (5)	5.8 (15)	
O <sub>d</sub> (5)	0.665 (2)	0.514 (3)	-0.252 (5)	6.0 (15)	O <sub>d</sub> (10)	0.560 (2)	0.639 (3)	0.708 (5)	6.4 (16)	
O <sub>d</sub> (5,N(2))	0.703 (1)	0.579 (2)	-0.094 (3)	1.4 (8)	O <sub>d</sub> (10,Co)	0.610 (1)	0.693 (2)	0.544 (3)	1.0 (8)	
O <sub>d</sub> (11,N(2))	0.697 (2)	0.673 (2)	0.164 (4)	2.8 (10)	O <sub>d</sub> (11,Co)	0.667 (1)	0.690 (2)	0.359 (3)	2.1 (9)	
N(1)	0.750	0.750	0.266 (9)	2.3 (24)	N(6)	0.555 (3)	0.363 (4)	0.074 (7)	6.5 (20)	
N(2)	0.750	0.675 (5)	-0.022 (8)	4.8 (23)	N(7)	0.303 (6)	0.750	0.201 (13)	10.4 (45)	
N(3)	0.250	0.750	0.457 (12)	4.9 (35)	N(8)	0.250	0.367 (4)	0.272 (8)	4.4 (23)	
N(4)	0.594 (3)	0.250	0.077 (7)	3.4 (20)	N(9)	0.327 (3)	0.387 (4)	0.402 (7)	6.5 (20)	
N(5)	0.553 (4)	0.250	0.263 (9)	6.4 (28)	N(10)	0.371 (3)	0.347 (4)	0.402 (7)	7.1 (22)	
O <sub>w</sub> (1)	0.700 (3)	0.750	0.538 (7)	5.0 (20)	O <sub>w</sub> (4)	0.524 (2)	0.418 (2)	0.240 (4)	4.1 (12)	
O <sub>w</sub> (2)	0.750	0.644 (2)	0.467 (4)	1.3 (11)	O <sub>w</sub> (5)	0.620 (2)	0.350 (3)	0.294 (5)	7.1 (18)	
O <sub>w</sub> (3)	0.422 (2)	0.516 (2)	0.394 (5)	5.5 (14)	O <sub>w</sub> (6)	0.655 (3)	0.750	0.000 (7)	5.0 (20)	

<sup>a</sup> The esd's in parentheses refer to last decimal places. <sup>b</sup> Symmetry code: (I)  $x, y, z$ ; (II)  $1/2 - x, y, z$ ; (III)  $x, 1/2 - y, z$ ; (IV)  $1/2 - x, 1/2 - y, z$ .

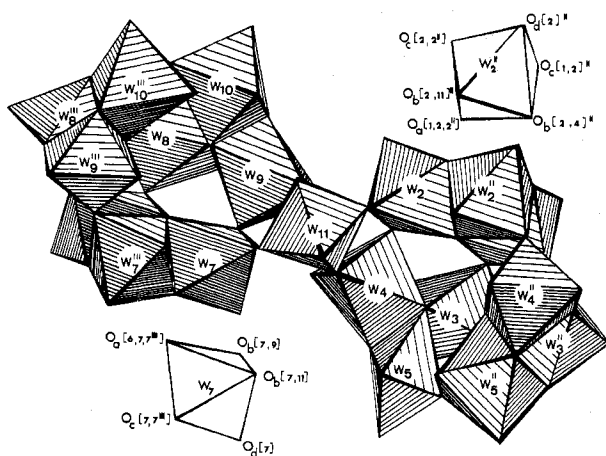


Figure 2. Polyhedral model and tungsten numbering of the two independent  $\text{AsW}_9\text{O}_{33}$  units linked by a  $\text{W}(11)$  octahedron.

and imaginary parts of the anomalous dispersion were introduced for W and As atoms.

### Results

The results are interpreted by the occurrence on L of two independent types of coordination sites: a cryptant site S1 and four coordinative sites S2 (Figure 1).

Four kinds of oxygen atoms are to be considered: oxygens bridging tungsten atoms and the central As heteroatom (referred to as  $\text{O}_a$ ), oxygens bridging two tungsten atoms (referred to as  $\text{O}_b$  when they belong to two different  $\text{W}_3\text{O}_{13}$  groups and  $\text{O}_c$  when they belong to the same  $\text{W}_3\text{O}_{13}$  group), and oxygens linked to only one tungsten (referred to as  $\text{O}_d$ ). Numbers in parentheses refer to the W atoms to which they are linked. An atom A related by the second symmetry code II is  $\text{A}^{\text{II}}$  (Figure 2).

**General Description of the Complex.** In the complex the ligand L consists of four  $\text{AsW}_9\text{O}_{33}$  subunits related through a pseudo 4 axis and joined up by four extra  $\text{WO}_6$  octahedra  $\text{W}(11)$ . Each  $\text{W}(11)$  atom joins two  $\text{AsW}_9\text{O}_{33}$  subunits by sharing two cis oxygen atoms with each one. The unshared oxygen atoms ( $\text{O}_d(11)$ ,  $\text{O}_d(11,\text{Co})$  in cis position) and the symmetry-related ones define the central site S1. These same oxygen atoms also define together with two oxygen atoms of each  $\text{AsW}_9\text{O}_{33}$  subunit ( $\text{O}_d(10,\text{Co})$ ,  $\text{O}_d(10,\text{Co})^{\text{II}}$  or  $\text{O}_d(5,\text{N}(2))$ ,  $\text{O}_d(5,\text{N}(2))^{\text{III}}$  and symmetry-related ones) the S2 sites.

In the actual crystal structure, an  $\text{NH}_4^+$  ion fills the S1 site, two "opposed" (see below) S2 sites are occupied by  $\text{Co}^{2+}$  and the two others are in interaction with  $\text{NH}_4^+$  ions. Thus, we have to consider two independent  $\text{AsW}_9\text{O}_{33}$  subunits, one including  $\text{Co}^{2+}$  and the other  $\text{NH}_4^+$ .

**The  $\text{AsW}_9\text{O}_{33}$  Subunit.** Each  $\text{AsW}_9\text{O}_{33}$  subunit consists of a Keggin type assemblage<sup>17</sup> of three  $\text{W}_3\text{O}_{13}$  groups around the As heteroatom which has a trigonal surrounding. The lone pair of  $\text{As}^{\text{III}}$  is directed toward the opening of the  $\text{AsW}_9\text{O}_{33}$  structure. This structure has been referred to as  $\alpha\text{-B-XW}_9$  by Hervé and Tézé.<sup>18</sup>

The equivalent bond distances are listed in Table II for the two independent half groups  $\text{AsW}_9\text{O}_{33}$  of the asymmetric unit. There are no particular variations between the two sets of values. The mean values are, for  $\text{W-O}_a$ , 2.38 Å, for  $\text{W-O}_b$ , 1.93 Å, for  $\text{W-O}_c$ , 1.93 Å, and, for  $\text{W-O}_d$ , 1.71 Å. These distances agree with those found in other Keggin like structures.<sup>19,20</sup> The  $\text{O}_b$  and  $\text{O}_c$  atoms lie in a square plane with

Table II. Interatomic Distances (Å)<sup>a</sup>

$\text{W}(1)\text{-O}_a(1,2,2^{\text{II}})$	2.47 (8)	$\text{W}(6)\text{-O}_a(6,7,7^{\text{III}})$	2.33 (6)
$\text{W}(1)\text{-O}_b(1,3)$	1.85 (5)	$\text{W}(6)\text{-O}_b(6,8)$	1.93 (5)
$\text{W}(1)\text{-O}_c(1,2)$	1.90 (5)	$\text{W}(6)\text{-O}_c(6,7)$	1.77 (4)
$\text{W}(1)\text{-O}_d(1)$	1.79 (6)	$\text{W}(6)\text{-O}_d(6)$	1.56 (6)
$\text{W}(2)\text{-O}_a(1,2,2^{\text{III}})$	2.31 (3)	$\text{W}(7)\text{-O}_a(6,7,7^{\text{III}})$	2.45 (4)
$\text{W}(2)\text{-O}_b(2,4)$	1.85 (6)	$\text{W}(7)\text{-O}_b(7,9)$	1.93 (5)
$\text{W}(2)\text{-O}_c(2,11)$	1.97 (4)	$\text{W}(7)\text{-O}_b(7,11)$	1.93 (4)
$\text{W}(2)\text{-O}_c(2,2^{\text{II}})$	1.98 (3)	$\text{W}(7)\text{-O}_c(7,7^{\text{III}})$	1.93 (3)
$\text{W}(2)\text{-O}_c(1,2)$	1.90 (4)	$\text{W}(7)\text{-O}_c(6,7)$	2.04 (4)
$\text{W}(2)\text{-O}_d(2)$	1.72 (4)	$\text{W}(7)\text{-O}_d(7)$	1.68 (5)
$\text{W}(3)\text{-O}_a(3,4,5)$	2.37 (4)	$\text{W}(8)\text{-O}_a(8,9,10)$	2.39 (3)
$\text{W}(3)\text{-O}_b(1,3)$	2.00 (5)	$\text{W}(8)\text{-O}_b(6,8)$	1.92 (5)
$\text{W}(3)\text{-O}_b(3,3^{\text{II}})$	1.93 (2)	$\text{W}(8)\text{-O}_b(8,8^{\text{III}})$	1.96 (2)
$\text{W}(3)\text{-O}_c(3,4)$	1.86 (4)	$\text{W}(8)\text{-O}_c(8,9)$	1.75 (4)
$\text{W}(3)\text{-O}_c(3,5)$	1.89 (4)	$\text{W}(8)\text{-O}_c(8,10)$	1.85 (6)
$\text{W}(3)\text{-O}_d(3)$	1.73 (5)	$\text{W}(8)\text{-O}_d(8)$	1.79 (4)
$\text{W}(4)\text{-O}_a(3,4,5)$	2.36 (4)	$\text{W}(9)\text{-O}_a(8,9,10)$	2.45 (4)
$\text{W}(4)\text{-O}_b(2,4)$	1.99 (6)	$\text{W}(9)\text{-O}_b(7,9)$	1.95 (5)
$\text{W}(4)\text{-O}_b(4,11)$	1.83 (4)	$\text{W}(9)\text{-O}_b(9,11)$	1.84 (4)
$\text{W}(4)\text{-O}_c(3,4)$	2.05 (4)	$\text{W}(9)\text{-O}_c(8,9)$	2.03 (4)
$\text{W}(4)\text{-O}_c(4,5)$	1.87 (5)	$\text{W}(9)\text{-O}_c(9,10)$	1.80 (5)
$\text{W}(4)\text{-O}_d(4)$	1.63 (5)	$\text{W}(9)\text{-O}_d(9)$	1.67 (6)
$\text{W}(5)\text{-O}_a(3,4,5)$	2.38 (4)	$\text{W}(10)\text{-O}_a(8,9,10)$	2.25 (4)
$\text{W}(5)\text{-O}_b(5,5^{\text{II}})$	1.97 (2)	$\text{W}(10)\text{-O}_b(10,10^{\text{III}})$	1.99 (3)
$\text{W}(5)\text{-O}_c(3,5)$	2.08 (4)	$\text{W}(10)\text{-O}_c(8,10)$	2.01 (6)
$\text{W}(5)\text{-O}_c(4,5)$	2.05 (5)	$\text{W}(10)\text{-O}_c(9,10)$	2.01 (5)
$\text{W}(5)\text{-O}_d(5)$	1.82 (7)	$\text{W}(10)\text{-O}_d(10)$	1.74 (7)
$\text{W}(5)\text{-O}_d(5,\text{N}(2))$	1.70 (4)	$\text{W}(10)\text{-O}_d(10,\text{Co})$	1.81 (4)
$\text{As}(1)\text{-O}_a(1,2,2^{\text{II}})$	1.77 (8)	$\text{W}(11)\text{-O}_b(2,11)$	1.86 (4)
$\text{As}(1)\text{-O}_a(3,4,5)$	1.79 (4)	$\text{W}(11)\text{-O}_b(7,11)$	1.90 (4)
$\text{As}(2)\text{-O}_a(6,7,7^{\text{III}})$	1.66 (6)	$\text{W}(11)\text{-O}_b(4,11)$	2.03 (4)
$\text{As}(2)\text{-O}_a(8,9,10)$	1.78 (4)	$\text{W}(11)\text{-O}_b(9,11)$	2.08 (4)
		$\text{W}(11)\text{-O}_d(11,\text{Co})$	1.83 (4)
		$\text{W}(11)\text{-O}_d(11,\text{N}(2))$	1.70 (5)

<sup>a</sup> The esd's in parentheses refer to last decimal places.

Table III

Bond Angles around Cobalt Atom (Deg)	
$\text{As}(2)\text{-Co-O}_d(11,\text{Co})$	94.7 (13)
$\text{As}(2)\text{-Co-O}_d(10,\text{Co})$	80.8 (11)
$\text{As}(2)\text{-Co-O}_w(1)$	172.9 (20)
$\text{O}_d(11,\text{Co})\text{-Co-O}_d(10,\text{Co})$	93.3 (17)
$\text{O}_d(11,\text{Co})\text{-Co-O}_w(1)$	90.3 (23)
$\text{O}_d(10,\text{Co})\text{-Co-O}_w(1)$	93.9 (23)
$\text{O}_d(11,\text{Co})\text{-Co-O}_d(11,\text{Co})^{\text{III}}$	90.8 (17)
$\text{O}_d(10,\text{Co})\text{-Co-O}_d(10,\text{Co})^{\text{III}}$	82.4 (16)
Bond Angles around Arsenic Atoms (Deg)	
$\text{O}_a(8,9,10)\text{-As}(2)\text{-O}_a(8,9,10)^{\text{III}}$	102 (2)
$\text{O}_a(8,9,10)\text{-As}(2)\text{-O}_a(6,7,7^{\text{III}})$	94 (2)
$\text{O}_a(8,9,10)\text{-As}(2)\text{-Co}$	103 (1)
$\text{O}_a(6,7,7^{\text{III}})\text{-As}(2)\text{-Co}$	152 (2)
$\text{O}_a(3,4,5)\text{-As}(1)\text{-O}_a(3,4,5)^{\text{II}}$	99 (3)
$\text{O}_a(3,4,5)\text{-As}(1)\text{-O}_a(1,2,2^{\text{II}})$	96 (2)

almost equivalent  $\text{W-O}_b$  and  $\text{W-O}_c$  bond lengths; orthogonal to this plane, there is a shorter bond ( $\text{W-O}_d$ ) corresponding to a multiple-bond character and a longer one ( $\text{W-O}_a$ ). The tungsten atom lies out of this plane on the side of  $\text{O}_d$ . The  $\text{O}_a\text{-W-O}_d$  mean angle value is  $168^\circ$ . The distances  $\text{As}(1)\text{-O}_a$  or  $\text{As}(2)\text{-O}_a$  are almost the same (mean value 1.78 Å) except for  $\text{As}(2)\text{-O}_a(6,7,7^{\text{III}})$  (1.66 Å). This small shortening is probably related to an interaction between  $\text{As}(2)$  and  $\text{Co}$  ( $\text{As}(2)\text{-Co} = 2.65$  Å) while an interaction cannot be considered between  $\text{As}(1)$  and  $\text{NH}_4^+$  ( $\text{As}(1)\text{-N}(2) = 3.88$  Å). Bond angle values around arsenic atoms are listed in Table III.

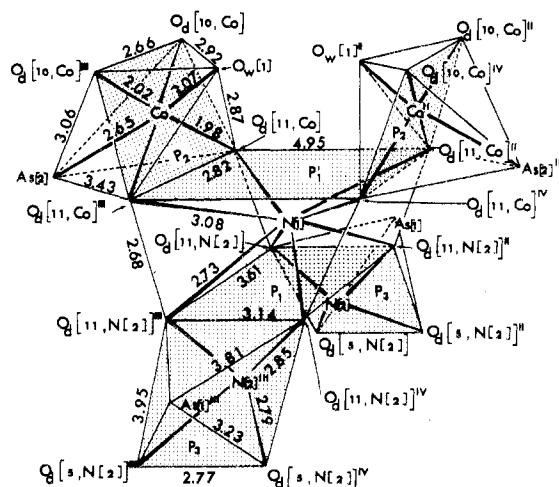
**The  $\text{WO}_6$  Bridging Octahedra ( $\text{W}(11)$ ).** The shared oxygen atoms  $\text{O}_b(2,11)$ ,  $\text{O}_b(4,11)$  and  $\text{O}_b(7,11)$ ,  $\text{O}_b(9,11)$  bridge each  $\text{AsW}_9\text{O}_{33}$  subunit through  $\text{W}(2)$ ,  $\text{W}(4)$  and  $\text{W}(7)$ ,  $\text{W}(9)$  which belong to different  $\text{W}_3\text{O}_{13}$  groups (Figure 2). The distances  $\text{W}(11)\text{-O}_b(2,11)$  (1.86 Å) and  $\text{W}(11)\text{-O}_b(7,11)$  (1.90 Å) are

(17) J. F. Keggin, *Proc. R. Soc. London, Ser. A*, **144**, 75 (1934).

(18) G. Hervé and A. Tézé, *Inorg. Chem.*, **16**, 2115 (1977).

(19) R. Allmann and H. D'Amour, *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.*, **141**, 161 (1975).

(20) F. Robert, A. Tézé, G. Hervé, and Y. Jeannin, *Acta Crystallogr., Sect. B*, **36**, 11 (1980).



**Figure 3.** Geometrical features of occupied coordination sites in the crystal. For clarity, only the coordinative oxygens and arsenics and the complexed cations are represented.

within the range of  $W-O_b$  and  $W-O_c$  mean values found for the  $AsW_9O_{33}$  subunits. The two others  $W(11)-O_b(4,11)$  and  $W(11)-O_b(9,11)$  are somewhat longer (2.03 and 2.08 Å, respectively). It can be noticed that they are trans to the shortest  $W(11)-O_d$  distances related to oxygen unshared with the  $AsW_9O_{33}$  subunits:  $W(11)-O_d(11, N(2))$  (1.70 Å) is nearly the  $W-O_d$  mean value, and  $W(11)-O_d(11, Co)$  (1.83 Å) is intermediate between  $W-O_d$  and  $W-O_b$  or  $W-O_c$ . The  $O-W(11)-O$  angle values are in the range 85 to 100° except for the angles  $O_b(4,11)-W(11)-O_b(2,11)$  (77.1°) and  $O_b(7,11)-W(11)-O_b(9,11)$  (77.0°) which intercept the  $AsW_9O_{33}$  subunits.

**The S1 Central Site Occupied by  $NH_4^+$ .** This site can be considered as a cryptant site. The coordinative oxygen define two parallel planes  $P_1$  ( $O_d(11, N(2))$  and symmetry related) and  $P_1'$  ( $O_d(11, Co)$  and symmetry related). The distance between these planes is 2.49 Å (Figure 3).

The central atom  $N(1)$  is nearer to  $O_d(11, N(2))$  (2.73 Å) than to  $O_d(11, Co)$  (3.08 Å), but  $N(1)$  is nearer to  $P_1$  (1.18 Å) than to  $P_1'$  (1.31 Å). This is related to the inequality of the corresponding dimensions of the rectangles which define  $P_1$  and  $P_1'$  (3.61 × 3.14 Å and 4.95 × 2.82 Å, respectively).

**The S2 Sites Occupied by  $Co^{2+}$ .** The four-coordinative oxygens  $O_d(10, Co)$  and  $O_d(11, Co)$  and symmetry-related ones define the  $P_2$  plane. The cobalt atom lies in this plane (Figure 3). The distances from Co to  $O_d(10, Co)$  and  $O_d(11, Co)$  are 2.02 and 1.98 Å, respectively. The cobalt is four-coordinated by the ligand  $NH_4L$  and has a fifth coordination position occupied by a molecule of water  $O_w(1)$  at a distance of 2.07 Å in a direction perpendicular to the  $P_2$  plane. Angle values around Co are listed in Table III.

About Co coordination, two possibilities can be considered:

The first is six-coordinate Co with a distorted octahedral geometry. An empirical evaluation of the direction for the lone pair of As(2) was performed in order to obtain the same angle value between this direction and each  $As(2)-O_a$  one. The evaluated direction for the lone pair is consistent with an interaction between As(2) and Co. A problem arises from the  $As(2)-Co$  distance (2.65 Å) which is greater than the usual covalent ones (from 2.3 to 2.45 Å) but considerably less than the nonbonded one (sum of the van der Waals radii of As and Co is about 3.95 Å). So, only a weak interaction can be assumed.

Second, we consider five-coordinate Co with a square-pyramidal geometry. Thus, it is very surprising that Co lies in the  $P_2$  plane. Generally, the metal lies from 0.3 to 0.6 Å above the basal plane inside the pyramid in most complexes. It is

**Table IV.** Equivalent Distances (Å) of Symmetry-Related W Atoms for the Two Crystallographically Independent  $AsW_9O_{33}$  Units and Their Differences (Å)

	$d(1)$	$d(2)$	$d(2) - d(1)$	
$W(1)-W(1)^{III}$	16.89	$W(6)-W(6)^{II}$	17.58	0.69
$W(2)-W(2)^{III}$	11.43	$W(7)-W(7)^{II}$	12.05	0.63
$W(3)-W(3)^{III}$	16.84	$W(8)-W(8)^{II}$	17.44	0.60
$W(4)-W(4)^{III}$	11.34	$W(9)-W(9)^{II}$	12.05	0.71
$W(5)-W(5)^{III}$	11.18	$W(10)-W(10)^{II}$	11.62	0.44
$As(1)-As(1)^{III}$	10.44	$As(2)-As(2)^{II}$	11.20	0.76

also difficult to explain that the  $As(2)-O_a(6,7,7^{III})$  distance is shorter than the other  $As(2)-O_a$  and  $As(1)-O_a$  ones by about 0.12 Å (Table II).

From these whole considerations a six-coordinate Co appears as the most suitable.

**The S2 Sites in Interaction with  $NH_4^+$ .** These two sites are defined by the four atoms  $O_d(5, N(2))$  and  $O_d(11, N(2))$  and symmetry-related ones which constitute the  $P_3$  plane. The  $N(2)$  atom of the  $NH_4^+$  ion lies 1.50 Å out of this plane. The distances  $N(2)-O_d(5, N(2))$  (2.79 Å) and  $N(2)-O_d(11, N(2))$  (2.85 Å) are consistent with an interaction between the ammonium ion and these four oxygens by hydrogen bonds (Figure 3).

## Discussion

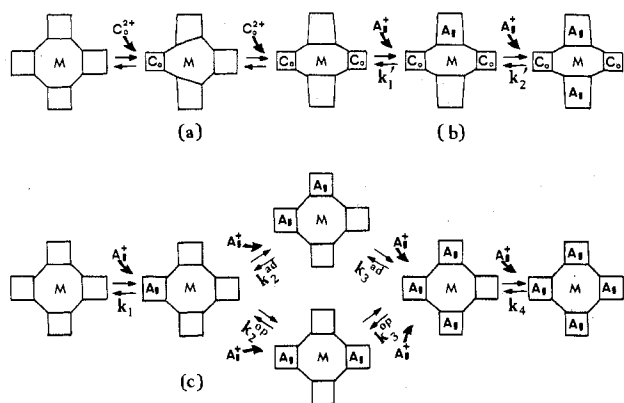
The structural results relevant to the complex  $NH_4LCO_2$  define the ligand geometry in the complex and the coordination sites S1 and S2. In this discussion, we analyze the deformation which affects L when two  $Co^{2+}$  ions are coordinated and the consequence of this deformation on the reactivity of the coordination sites.

**Conformational Changes in L due to  $Co^{2+}$  Coordination.** The ligand is defined by the association of four  $AsW_9O_{33}$  subunits through four tungsten atoms octahedrally surrounded. It may be assumed that, in the free ligand, these subunits are identical and are related by the symmetry elements  $4mm$  (point group  $D_{2d}$ ). In the complex the ligand symmetry is lowered (point group  $C_{2v}$ ). Two points may be noted: (1) the overall distortion of L (The distances between the  $AsW_9O_{33}$  symmetry-related subunits differ by about 0.64 Å (Table IV); note (Figure 3) also the dimensions of the rectangles which define the  $P_1$  and  $P_1'$  planes) and (2) the positions of the arsenic atoms with respect to the  $P_1$  and  $P_1'$  planes ( $As(1)$  lies 0.65 Å out of  $P_1$  in the side of  $N(2)$  while  $As(2)$  lies in the  $P_1'$  plane).

The conformational change of L is due to the coordination of two  $Co^{2+}$  ions and may be described in the following way: when  $Co^{2+}$  binds  $O_d(10, Co)$ ,  $O_d(11, Co)$ , and symmetry-related ones by code III, these oxygens move in the plane  $P_2$  toward  $Co^{2+}$  by about 0.4 Å so that the  $Co-O$  distance is close to 2.0 Å, characteristic of oxo complexes of  $Co^{2+}$ . In the free ligand, the  $W(10)-O_d(10, Co)$  and  $W(11)-O_d(11, Co)$  bonds are of  $W-O_d$  type (1.70 Å) (see Table II), and in the complex, the length of these bonds are 1.81 and 1.83 Å, respectively. This suggests that, besides this lengthening by about 0.10 and 0.15 Å, the  $W(11)$  and  $O_d(11, N(2))$  atoms move approximately in the same direction as  $O_d(11, Co)$ .

The transmission of these shifts to the  $AsW_9O_{33}$  subunits by the  $O-W(11)-O$  bridges explains the overall conformational changes observed.

**Selectivity of the Cryptant Site S1.** A first consequence of the ligand deformation in  $NH_4LCO_2$  is the significant distortion of the central site S1 (Figure 3). The calculated distance from the center of this site to  $O_d(11, N(2))$  or  $O_d(11, Co)$  is 2.92 Å, which is consistent with the highest affinity observed in the alkaline family for  $K^+$  or  $Rb^+$ . A suitable rule is that the stability is maximum when the metal-oxygen distance is close to the sum of the ionic radius of  $M^{n+}$  and the oxygen van der



**Figure 4.** Schematic model of interactions between the binding S2 sites of the ligand ML: (a) Co<sup>2+</sup> reacts successively only on two opposed S2 sites; (b) the modified vacant S2 sites react with Ag<sup>+</sup>; (c) with Ag<sup>+</sup>, no important conformational change occurs and the four sites are successively occupied. Two isomers of MLAG<sub>2</sub> can be considered; the dissociation constants  $k_i$  are indicated.

Waals radius. For Rb<sup>+</sup>, this sum is 2.88 Å and for NH<sub>4</sub><sup>+</sup>, 2.86 Å. We have previously pointed out<sup>2</sup> that, in the free ligand, the highest affinity is observed for K<sup>+</sup> for which the sum is 2.73 Å; this may be explained by the increase of the S1 site size because of Co<sup>2+</sup> complexation.

Moreover, it may be noted that the NH<sub>4</sub><sup>+</sup> ion N(1) is not equidistant from O<sub>d</sub>(11,N(2)) (2.73 Å) and O<sub>d</sub>(11,Co) (3.08 Å). If we assume that the NH<sub>4</sub><sup>+</sup> ion is perfectly tetrahedral with N–H distances of 1.0 Å, this position is suitable for hydrogen bonding with O<sub>d</sub>(11,N(2)) and O<sub>d</sub>(11,Co) even if the N–H bonds are statistically directed toward these oxygens or if hydrogen bonds are of bifurcated type.

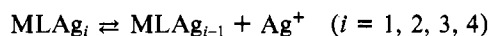
**Interactions between the S2 Coordination Sites Related to the Binding of a Metal Cation.** A second consequence of L conformational changes is an interaction between the four S2 sites which affects their reactivity. In the following discussion, two S2 sites joined by a W(11) atom are described as adjacent (ad) and, if not, as opposed (op).

**Effects of Co<sup>2+</sup> Coordination.** It can be explained why, in NH<sub>4</sub>LCo<sub>2</sub>, the cobalts occupy opposed positions and why the coordination of two further Co<sup>2+</sup> in the remaining vacant sites does not occur. The formation of a stable oxo complex of Co<sup>2+</sup> needs a Co–O bond length of about 2.0 Å that agrees with the Co–O distances in the occupied sites. In the two vacant S2 sites of the complex NH<sub>4</sub>LCo<sub>2</sub>, the calculated distance from the center of these sites (in the P<sub>3</sub> plane) to the ligating oxygens O<sub>d</sub>(5,N(2)) or O<sub>d</sub>(11,Co) is 2.49 Å. The coordination of Co<sup>2+</sup> in these sites would involve a large shift of these ligating oxygens which cannot occur because of the “clamping” of the ligand by the previously coordinated Co atoms. In the same way, the linkage of one Co<sup>2+</sup> ion on one of the four vacant S2 sites of the ligand ML alters this site and induces changes in the conformation of the two adjacent S2 sites while the opposed one remains unchanged. Thus, only this latter site can bind another Co<sup>2+</sup> ion.

Thus, for their reaction with Co<sup>2+</sup> ions and generally, with the first-row transition metals Z<sup>n+</sup>, the four S2 sites of the ligand are not independent; only opposite sites are independent, and a negative cooperativity is observed for the two adjacent ones. These interactions between sites of a molecule are analogous to those observed on oligomeric proteins, which have been described as allosteric effects. The effects observed here, schematically represented (Figure 4a), are coherent with the sequential model proposed by Koshland.<sup>21</sup>

**Effects of Ag<sup>+</sup> Coordination.** It has been previously shown that the S2 sites can also be occupied by Ag<sup>+</sup> cations.<sup>2</sup> The behaviors of Ag<sup>+</sup> and Co<sup>2+</sup> are different because Ag<sup>+</sup> can react with the two vacant sites of MLCo<sub>2</sub> (Figure 4b) or with the four sites of ML (Figure 4c). This behavior is related to the Ag–O bond length (usually 2.4 or 2.6 Å); therefore the formation of stable complexes with Ag<sup>+</sup> does not induce large changes in the size of S2 sites and, consequently, in the conformation of the ligand (in ML or MLCo<sub>2</sub>). This formation of the MLAG<sub>4</sub> complex indirectly supports our early assumption: the ligand in ML is more symmetrical than in MLCo<sub>2</sub>.

A quantitative study of the Ag<sup>+</sup> coordination can be attempted from the analysis of the potentiometric titration curve of the ligand ML by Ag<sup>+</sup>.<sup>2</sup> This curve showed only one equivalent point for four Ag<sup>+</sup> ions added to ML; no intermediate complex was quantitatively made. The reaction of Ag<sup>+</sup> with the ligand occurs according to the successive equilibria



We can define the corresponding conditional dissociation constants

$$K_i = [\text{MLAg}_{i-1}]a_{\text{Ag}^+}/[\text{MLAg}_i]$$

written with the concentration for the complexes and the activity for Ag<sup>+</sup>. Because of the high charge of the compounds involved, the ionic strength can be considered as unchanged during the titration. Using the reaction scheme of Figure 4c, which takes into account the existence of two MLAG<sub>2</sub> isomers (adjacent or opposite S2 sites occupied), we may obtain the following relation between the number  $x$  of Ag<sup>+</sup> added per mole of ligand and the activity of Ag<sup>+</sup>:

$$x = A(1-x)a_{\text{Ag}^+} + B(2-x)a_{\text{Ag}^+}^2 + C(3-x)a_{\text{Ag}^+}^3 + D(4-x)a_{\text{Ag}^+}^4$$

where  $A = 1/k_1$ ,  $B = (1/k_2^{\text{ad}} + 1/k_2^{\text{op}})/k_1$ ,  $C = 1/k_1k_2^{\text{ad}}k_3^{\text{ad}} = 1/k_1k_2^{\text{op}}k_3^{\text{op}}$ , and  $D = 1/k_1k_2^{\text{ad}}k_3^{\text{ad}}k_4 = 1/k_1k_2^{\text{op}}k_3^{\text{op}}k_4$ . Approximate values of  $A$ ,  $B$ ,  $C$ , and  $D$  were obtained from potentiometric data by solving the above equations. Then least-squares refinement gave accurate values used in further calculations. In order to obtain the successive constants  $k_i$ , we propose a simple mathematical model in which each  $pK_i$  is written as the sum of four terms:

$$pK_i = pK + \Delta_i(\text{stat}) + \Delta_i(\text{elec}) + \Delta_i(\text{conf})$$

which takes into account (1) the intrinsic affinity of a site ( $pK$ ), supposed isolated, corresponding to the equilibrium  $\text{S2Ag}^+ \rightleftharpoons \text{S2} + \text{Ag}^+$ , (2) a statistical effect due to the existence of several identical sites [If only this effect was involved, the relations between the  $k_i$  would be

$$k = 4k_1 = k_2^{\text{op}}/2 = k_2^{\text{ad}} = 2k_3^{\text{op}} = k_3^{\text{ad}} = k_4/4$$

The values of  $\Delta_i(\text{stat}) = \log \alpha_i$  are deduced from these relations of the type  $k = \alpha_i k_i$ , (3) an electrostatic effect between sites which expresses that the positive charge of the cation in a S2 site decreases the affinity of the other vacant sites [In this simple model we assume that the electrostatic interactions do not depend on the location of the sites (the distances between adjacent or opposed sites are not very different) and are the same for all the successive complexes MLAG<sub>*i*</sub>. Thus, each coordinated Ag<sup>+</sup> introduces an electrostatic increment  $\Delta(\text{elec})$ ;  $\Delta_i(\text{elec})$  can be evaluated by  $\Delta_i(\text{elec}) = (i-1)\Delta(\text{elec})$ ], and (4) a conformational effect which expresses that the occupation of a site induces changes in the conformation of the adjacent sites and, consequently, in their affinity (conformational in-

(21) D. E. Koshland Jr., and K. E. Neet, *Annu. Rev. Biochem.*, **37**, 359 (1968).

Table V

ligand	const	$pk_i = pk + \Delta(\text{stat}) + (i-1)\Delta(\text{elec}) + j\Delta(\text{conf})$	obsd	calcd <sup>a</sup>
MLCo <sub>2</sub>	$pk'_1$	$pk' + 0.30$	8.85	
	$pk'_2$	$pk' - 0.30 + \Delta(\text{elec})$	7.95	
	$pk_1$	$pk + 0.60$	9.08	
	$pk_4$	$pk - 0.60 + 3\Delta(\text{elec}) + 2\Delta(\text{conf})$	6.78	
ML	$pk_2^{\text{op}}$	$pk - 0.30 + \Delta(\text{elec})$		7.88
	$pk_2^{\text{ad}}$	$pk + \Delta(\text{elec}) + \Delta(\text{conf})$		8.08
	$pk_3^{\text{op}}$	$pk + 0.30 + 2\Delta(\text{elec}) + 2\Delta(\text{conf})$		7.98
	$pk_3^{\text{ad}}$	$pk + 2\Delta(\text{elec}) + \Delta(\text{conf})$		7.78
	$\log(1/k_2^{\text{op}} + 1/k_2^{\text{ad}})$		8.24	8.29
	$pk_2 + pk_3$ (op or ad)		15.81	15.86

<sup>a</sup> The values in this column were calculated from the equation in the previous column, by using the following values:  $pk' = 8.55$ ,  $\Delta(\text{elec}) = -0.30$ ,  $pk = 8.48$ , and  $\Delta(\text{conf}) = -0.10$ , which were obtained from the observed values of  $pk'_1$ ,  $pk'_2$ ,  $pk_1$ , and  $pk_4$ , respectively.

crement  $\Delta(\text{conf})$ ) but not in the affinity of the opposite ones [Thus, the value of  $\Delta_i(\text{conf})$  can be evaluated by  $\Delta_i(\text{conf}) = j\Delta(\text{conf})$  in which the parameter  $j$  for a site is equal to the number of occupied adjacent sites (0, 1, or 2).]

With use of this model, the intrinsic  $pk$  value 8.48 has been obtained from  $\log A = pk_1 = pk + 0.60$ , since only the statistical term is involved (Table V). The value of  $\Delta(\text{elec})$  (-0.30) has been deduced from the dissociation constants of  $\text{Ag}^+$  complexes of  $\text{MLCo}_2$  previously reported:<sup>2</sup> in  $\text{MLCo}_2\text{Ag}_2$ , both  $\text{Ag}^+$  ions are in two opposite S2 sites and only statistical and electrostatic effects are involved; as a first approximation, it has been assumed that the electrostatic interactions in ML and  $\text{MLCo}_2$  are the same. The conformational term  $\Delta(\text{conf})$  (-0.10) has been deduced from the value of  $pk_4$  ( $\log(D/C)$ ). Finally  $k_2$  and  $k_3$  (adjacent and opposite) have been calculated. Their values are in good agreement with the experimental values of  $k_2^{\text{op}} + k_2^{\text{ad}}$  and  $k_2k_3$ . Moreover, the values of  $\Delta(\text{elec})$  (-0.30) and  $\Delta(\text{conf})$  (-0.10) show that, in the  $\text{Ag}^+$  reaction, there is a low negative cooperativity between sites. The behavior of  $\text{Co}^{2+}$  can be described with the same model; the high negative cooperativity observed between a site and the adjacent ones involves a largely negative value of  $\Delta(\text{conf})$ .

## Conclusion

This study shows that the polyanionic ligand  $(\text{As}_4\text{W}_{40}\text{O}_{140})^{28-}$  results from the connection of four identical  $\text{AsW}_9\text{O}_{33}^{9-}$  subunits through four  $\text{WO}_6$  extra groups. The mechanism of formation of this species is not known. However, it can be noticed that each subunit has the so-called "α-B-type" 9-tungstoheteropolyanionic structure,<sup>18</sup> i.e., three  $\text{W}_3\text{O}_{13}$  groups around the heteroatom, using the three bonds of  $\text{As}^{\text{III}}$  according to the pyramidal geometry. This is different from the so-called "A-type" 9-tungstoheteropolyanionic structure observed with  $\text{Si}^{\text{IV}}$ , i.e., on  $\text{W}_3\text{O}_{13}$  group and three  $\text{W}_2\text{O}_{10}$  groups around the heteroatom, using the four bonds of  $\text{Si}^{\text{IV}}$  according to a tetrahedral geometry.<sup>22</sup> We have reported that this latter structure can be completed by one  $\text{W}_2\text{O}_{11}$  group (formation of 11-tungstoheteropolyanionic structure) or one  $\text{W}_3\text{O}_{15}$  group leading to the well-known closed "Keggin structure".<sup>23,24</sup> In the "α-B-type"  $\text{AsW}_9\text{O}_{33}$  subunit structure, the lone pair of electrons directed toward the opening of the structure prevents  $\text{As}^{\text{III}}$  from nucleophilic attack by the oxygen ligands of tungstic groups. Thus, this structure cannot be closed as the "A-type", and we observe an association in which the electron pair remains free. Another compound, the tungstoantimonate  $(\text{Sb}_9\text{W}_{21}\text{O}_{86})^{19-}$ , has a structure in agreement with these views: three subunits are linked by two  $\text{Sb}_3\text{O}_7$  extra groups, all the  $\text{Sb}^{\text{III}}$  having a pyramidal geometry with a lone pair.<sup>10</sup>

In these two ligands, the association of several subunits defines two types of coordination sites: (i) a central cryptant site S1 with a selectivity for alkaline or alkaline-earth cations depending on its size; (ii) several external coordinative sites S2, which react with transition- and post-transition-metal cations. In the title compound, the flexibility of the association allows conformational changes of the ligand which involve interactions between S2 sites, depending on their relative positions. This is an inorganic example of the allosteric effect observed with biological oligomeric macromolecules such as proteins.

**Registry No.**  $(\text{NH}_4)_{23}(\text{NH}_4\text{As}_4\text{W}_{40}\text{O}_{140}\text{Co}_2(\text{H}_2\text{O})_2)$ , 73261-70-8.

**Supplementary Material Available:** A listing of structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

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