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Square Pyramidal Complexes of Divalent Cations of the First Transition Row with the 20-Tungsto-2-arsenate(III): Synthesis, Visible and E.S.R. Spectra

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The synthesis of 20-tungsto-2-arsenate(III) is reported. This compound is a rigid tetradentate ligand and square pyramidal complexes are obtained with divalent cations of the first transition metal period. Stabilities and electronic spectra of these complexes are discussed. The E.S.R. spectrum of the vanadium(IV) complex is analyzed and compared with spectra of other polyoxotungstic complexes.

Introduction

Recently many complexes of five-coordinated cations of the first transition row have been described [1, 2]. Two types of structures are observed, square-pyramidal and trigonal-bipyramidal, the latter being the most common. One way to obtain square pyramidal complexes is to dispose of rigid tetradentate ligands in which the coordinative atoms have a square planar geometry. Such a geometry is observed in the polyoxotungstic ligand $[As_2^{III}W_{20}O_{68}(H_2O)]^{10-}$ in which the lone pair of electrons on the arsenic atoms implies a specific structure. We report here the synthesis of this ligand and of its complexes with the cations of the first transition row and discuss their stabilities, visible and E.S.R. spectra in correlation with the environment of the metal.

Experimental

Preparation of Compounds

$K_{10}[As_2W_{20}O_{68}(H_2O)]\cdot nH_2O$ $(21 \leqslant n \leqslant 23)$

The potassium salt of the 19-tungsto-2-arsenate-(III), obtained following the procedure of Tourné [3] (60 g), was stirred with 400 ml of water. Hydrochloric acid 12 *M* (10 ml) was added progressively and the solution boiled for fifteen minutes. Potassium hydrogenocarbonate was then added until pH ≈ 2. The precipitate was eliminated and the solution kept for two days at room temperature. Crystals of the product were filtered off.

$K_8[Z(H_2O)As_2W_{20}O_{68}(H_2O)]\cdot nH_2O$ $(23 \leqslant n \leqslant 25;$ $Z = Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, VO^{2+})$

15 g of the potassium salt of the 20-tungsto-2-arsenate were dissolved in 40 ml of water at 60 °C and 6 ml of a solution of $Z(NO_3)_2$ 0.5 *M* was added. The resulting solution was kept at 60 °C for ten minutes and then left at room temperature for one day. Crystals of the complexes were filtered off. The Ni(II) complex was prepared in presence of a large excess of metal.

Analyses

Samples of products were boiled with an excess of sodium hydroxide up to total decomposition; analyses were carried out on the resulting solutions. Tungsten was weighted as WO_3 after precipitation by cinchonin and ignition at 600 °C. Arsenic(III) was titrated by I_2 in an excess of hydrogenophosphate in order to wholly complex the tungsten. Cobalt(II) was titrated by hexacyanoferrate(III), Mn(II) by spectrophotometry as permanganate, Ni(II) by gravimetry with dimethylglyoxime, Zn(II), Cu(II) and vanadium by polarography, respectively in 1 *M* NaOH, 2 *M* ammoniacal buffer and 1 *M* acetic buffer in presence of pyrocatechol.

Physical Measurements

The molecular weight of tungstoarsenate was estimated in solution by analytical ultracentrifugation with a Beckman type E centrifuge with a Schlieren optical system. Measures were performed in NaCl 0.2 *M* at 2×10^{-2} and 4×10^{-2} *M* of tungsten. The rotation speed was 26,000 rpm and results were discussed according to Archibald's method.

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ESR spectra were recorded on an X band Jeol ME 3X spectrometer with a TE011 mode cylindrical cavity. Low temperature experiments were performed by blowing cold nitrogen gas through the cavity. The magnetic field was measured with a proton NMR probe and the microwave frequency with a wavemeter giving an accuracy of ± 1 MHz. The low temperature spectrum was simulated using a computer program with axially symmetric g and A tensors.

Study of Complexes

Relative stabilities of complexes were determined *versus* those of cobalt by addition of increasing quantities of Z^{2+} ions to a 3×10^{-2} *M* solution of the Co(II) complex. Competition equilibrium was established after two days.

The substitution reaction of the water molecule linked to Z in the complex by adenosine was studied spectrophotometrically by Job's method.

Results

The analysis of the potassium salt of the tungstoarsenate (W/As $\simeq$ 10 and K/As $\simeq$ 5) and its molecular weight (about 6,000) lead to formulate the anion as $[As_2W_{20}O_{68}(H_2O)]^{10-}$. This anion is stable in solution between pH 2 and 4. Below pH 2, it is hydrolysed to 21-tungstodiarsenate [4, 5] and, above pH 4, to 19-tungstodiarsenate [6]. It can be characterized in solution by polarography (two waves at –0.70 and 0.89 V *versus* saturated calomel electrode, at pH 3.5) and spectroscopy (U.V spectrum with a shoulder at 240 nm, $\epsilon = 75{,}000$).

Formation and Stabilities of the Complexes

The 20-tungstodiarsenate (hereafter noted L) reacts with Z^{2+} cations of the first transition row, giving strongly colored complexes. This property allows a spectrophotometric study of the reaction stoechiometry. For example, the titration curve at 600 nm of L by Co^{2+} shows a clear break for the ratio $Co^{2+}/L = 1$. Analyses of the potassium salts agree with the formation of the complexes 1/1 following the equation:

$$[As_2W_{20}O_{68}(H_2O)]^{10-} + [Z(H_2O)_6]^{2+} \rightleftarrows [Z(H_2O)As_2W_{20}O_{68}(H_2O)]^{8-} + 5H_2O \quad (1)$$

With V(IV), analytical results show that the water molecule linked to Z is replaced by an oxygen atom (V=O).

Electronic spectra of the complexes (Fig. 1) are strongly enhanced in comparison with aquo-ion ones. For example, the Co^{2+} complex ($Co(H_2O)L$) is green with an intense band at 16.1 kK ($\epsilon = 30$).

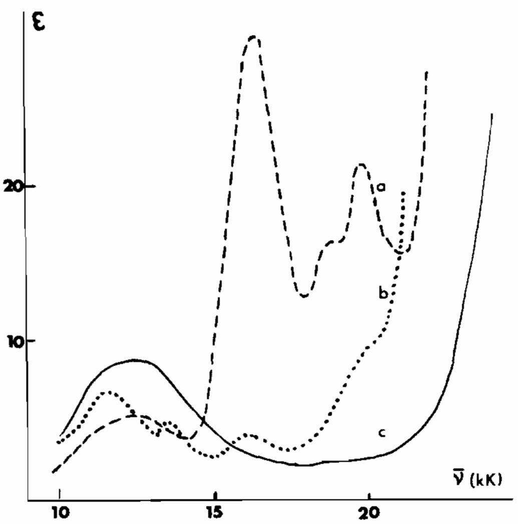

Fig. 1. Electronic spectra of the $Z(H_2O)L$ complexes: (a) Co^{2+}; (b) Ni^{2+}; (c) Cu^{2+}.

Relative stabilities of the complexes were determined from competition experiments between Co^{2+} and the other Z^{2+} cations:

$$[Co(H_2O)L]^{8-} + [Z(H_2O)_6]^{2+} \rightleftarrows [Z(H_2O)L]^{8-} + [Co(H_2O)_6]^{2+} \quad (2)$$

Assuming that no free ligand remains in presence of an excess of Z^{2+} cations, the concentration of $Z(H_2O)L$ was obtained from:

$$[Z(H_2O)L] = \frac{A - \epsilon_Z[Z]_0 - \epsilon_{Co(H_2O)L}[Co(H_2O)L]_0}{\epsilon_{Z(H_2O)L} + \epsilon_{Co} - \epsilon_{Co(H_2O)L} - \epsilon_Z}$$

where A is the absorbance of the solution at 620 nm, measured in a cell of 1 cm, $[Z]_0$ and $[Co(H_2O)L]_0$ are the initial concentrations of Z^{2+} and of the cobalt complex, and ϵ_i the absorptivity of the species i. The calculated equilibrium constants K_2 are listed in Table I.

TABLE I. Equilibrium Constants of Reactions 2 and 3.

Z	Mn	Co	Ni	Cu	Zn
K_2	2.3	1	0.05	11	3.2
K_3	[a]	3200[b]	1650[b]	1000[c]	500[b]
ΔE_2	$-0.16\ e_\sigma$	0	$0.28\ e_\sigma$	$-0.44\ e_\sigma$	$-0.16\ e_\sigma$

[a] No change in the electronic spectrum on addition of ADO. [b] pH = 3.6. [c] pH = 2.8.

Action of Purine Nucleosides on the Complexes

The coordination sphere of Z^{n+} transition metal cations complexed by polyoxotungstic ligands is generally completed by a water molecule in aqueous solution and substitution reactions of this molecule by various ligands have been observed [7]. Similar experiments were performed with $Z(H_2O)L$ complexes, using the two analogous nucleosides adenosine and guanosine.

Using Job's method, the formation of 1/1 complexes was evidenced with adenosine (ADO), following the equation:

$$Z(H_2O)L + ADO \rightleftharpoons Z(ADO)L + H_2O \qquad (3)$$

Equilibrium constants K_3 are listed in Table I. On the contrary, no reaction was observed with guanosine.

E.S.R. Spectra

The E.S.R. spectrum of the complex VOL in aqueous solution at 72 °C is typical of a V^{4+} ion and exhibits the eight hyperfine lines due to coupling of the unpaired electron ($S = 1/2$) with the nuclear spin ($I = 7/2$) of the 100% abundant ^{51}V isotope. This spectrum can be described by the usual isotropic spin-hamiltonian

$$H = g_0 \cdot H \cdot S + A_0 SI$$

The measured g_0 and A_0 values are 1.945 and -93.7×10^{-4} cm^{-1}. The frozen solution spectrum (Fig. 2) exhibits the perpendicular and parallel features typical of a V^{4+} ion in an axially distorted ligand field. No orthorombic component can be seen in the spectrum, showing that the orthorombic distortion of the ligand field must be smaller than the experimental linewidth ($\Delta H_{/\!/} = 12$ G, $\Delta H_{\perp} = 15$ G). The symmetry around the V^{4+} ion can then be approximated to C_{4v}, leading to the following spin-Hamiltonian:

$$\hat{H} = g_{/\!/}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + A_{/\!/} S_z I_z + \\ + A_{\perp}(S_x I_x + S_y I_y)$$

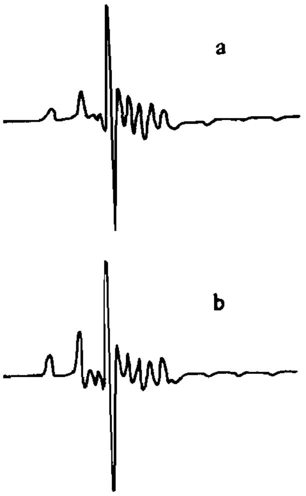

Fig. 2. E.S.R. spectrum of the vanadium complex in aqueous frozen solution. H = 3450 ± 1000 G; (a) experimental, (b) simulated.

where z is taken along the main axis of the axially symmetric g and A tensors. The best fit between experimental and simulated spectra was obtained for the following values: $g_{/\!/} = 1.869$, $g_{\perp} = 1.973$, $A_{/\!/} = -175 \times 10^{-4}$ cm^{-1}, $A_{\perp} = -57 \times 10^{-4}$ cm^{-1}.

Discussion

Coordination of Z in the Complexes

In the following, we analyze the properties of the $Z(H_2O)L$ complexes with regard to the symmetry of the environment of Z, that is, imposed by the structure of L. The obtention of L by hydrolysis of $(As_2W_{21}O_{69}(H_2O))^{6-}$, *i.e.* by loss of a WO^{4+} group, allows us to propose for L a structure deriving from 'As_2W_{21}', which has been established by X-ray diffraction [5]. This assumption is supported by the strong analogy between the infra-red spectra of these two polyoxotungstates. The 20-tungstodiarsenate(III) can be seen as two AsW_9O_{33} units linked by two tungsten atoms (Fig. 3). One tungsten (W_A) is pentacoordinated with an axial double bond $W_A{=}O$ outside the frame, the other (W_B) is hexacoordinated with an axial disposition $O{=}W_B{-}H_2O$ (the water molecule being outside and the oxygen atom inside the frame).

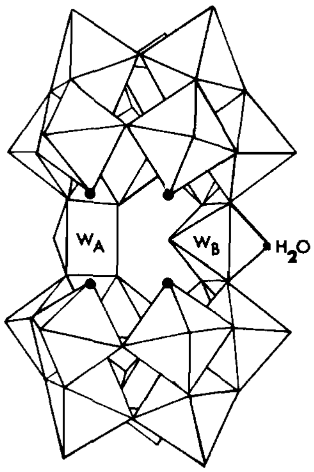

Fig. 3. Polyhedral model of the proposed structure of the 20-tungstodiarsenate. Arsenic atoms are not shown. The four coordinative oxygen atoms are marked.

By this structure the 20-tungstodiarsenate(III) is a tetradentate ligand via four oxygen atoms in an approximate square planar geometry. The oxygen atom on W_B precludes the presence of any other molecule within the structure. So, a complexed Z^{n+} metal cation can be either tetracoordinated (square planar) or pentacoordinated (square pyramidal) if there is a ligand L′ on its external axial position.

In fact, the mechanism of formation of $Z(H_2O)L$ is complex: when L is added to a solution of Z^{2+}

cations, a first compound is instantaneously formed (for example, the electronic spectrum of Co^{2+}_{aq} is enhanced without important modifications) and, then, transforms slowly to the final complex. Attempts to isolate the intermediate failed. We propose the mechanism of Fig. 4: in the first step, the complex $Z(H_2O)_4L$ is rapidly formed, with Z^{2+} linked to L via two *cis* positions. The following formation of the final complex, where Z is five coordinated, involves the breaking of a $Z-H_2O$ bond. This second step is rate determining for the overall process.

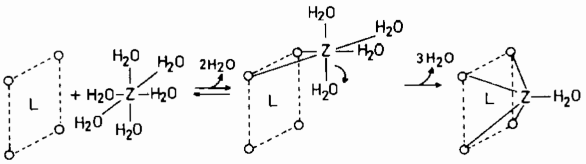

Fig. 4. Proposed mechanism of formation of the complexes.

With the divalent cations of the first transition row, a water molecule as L′ is clearly evidenced by its substitution by adenosine (ADO). There is a dichotomy in the binding of metal ions to the purine base portion of nucleosides. Both N(1) in the six membered ring and N(7) in the imidazole ring of adenosine or guanosine serve as donors to metal ions in solution [8]. The mode of coordination of ADO to Z in Z(ADO)L complexes can be deduced from two observations: (i) the binding of ADO is pH dependent between pH 2 and 4 (for example, for Co^{2+}, the equilibrium constant of eqn. 3 is 3200 at pH = 3.6 and 1700 at pH = 2.7); (ii) No substitution of water was observed in the presence of guanosine, even in large excess. The pK_a corresponding to N(1) protonation is about 3.5 for adenosine and N(7) can be protonated only in strongly acid solution. Then, the pH dependence of reaction 3 around pH = 3 involves a coordination of adenosine to Z via N(1). This is in agreement with the previously reported observation that, when one coordination position is only available on a metal cation, the binding via N(1) is favored with respect to N(7) [9]. This also explains why guanosine does not react: the pK_a corresponding to the protonation of N(1) is about 9.2: it is protonated in all the pH range of stability of the $Z(H_2O)L$ complexes and it can be expected that the equilibrium constant value is very weak near pH 3.

With the V(IV) complex, the external ligand L′ cannot be evidenced by substitution reactions, but analytical results showed that an oxygen atom is present. So we can assume that in all the complexes studied the environment of the metal Z is of square pyramidal type.

Relative Stabilities of the Complexes

The most important feature of the K_2 values (Table I) is the weak stability of the nickel complex. We have attempted to correlate this result with the repartition of electrons in d orbitals, that is by computing the ligand field stabilization change associated to the reaction:

$$\Delta E_2 = E(Z(H_2O)L) + E(Co) - E(Co(H_2O)L) - E(Z) \qquad (4)$$

ΔE_2 was calculated using the angular overlap model [10], with the following assumptions: (a) the complexes $Z(H_2O)L$ have a regular square pyramidal geometry with Z in the plane of the four equatorial oxygen atoms; (b) the e_σ and e_π parameters have the same values for all the metals and for oxygen and water; (c) ΔE_2 was finally expressed in e_σ units only, with a e_π/e_σ ratio of 0.2, as proposed by Ciampolini for water [1]. The calculated ΔE_2 values listed in Table I are compared with experimental pK_2 values (Fig. 5) (the entropy change of reaction 4 was assumed to be very small): the two curves are remarkably similar.

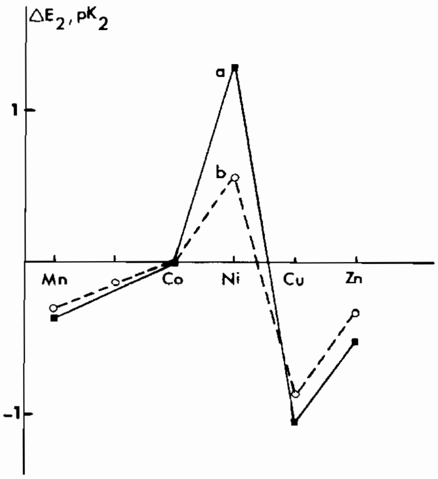

Fig. 5. Relative stabilities of the $Z(H_2O)L$ complexes. (a) pK_2, (b) ΔE_2. The ordinate scale is relative to pK_2 and the magnitude of the variations of ΔE_2 has been adapted in order to obtain the best fit.

Electronic Spectra of Co^{II} and Ni^{II} Complexes

Assignments of the absorption bands can be proposed using a weak field model, as described by Ciampolini [1] for pentacoordinated complexes. Three parameters are considered: the angle $H_2O_{ax}-Z-O_{eq}$, noted α, $D_q(ax)$ and $D_q(eq)$. The experimental spectra of $Co(H_2O)L$ and $Ni(H_2O)L$ can be correctly described with the values of these parameters and assignments listed in Table II.

Vanadium(IV) Complex

The g and A values of V(IV) in VOL can be compared with the corresponding ones in other polyoxotungstic complexes, such as $VO(XW_{11}O_{39})^{n-}$ (X = Si,

TABLE II. Proposed Assignments of Absorption Bands of Co^{II} and Ni^{II} Complexes.

Complex	ν (kK)	Assignments	Parameters
$Co(H_2O)L$	12.3	$^4A_2(F) \rightarrow {^4B_1(F)}$	$\alpha = 100°$
	16.1	$^4A_2(F) \rightarrow {^4E(P)}$	$D_q(ax) = D_q(eq)$
	18.9	spin forbidden	= 0.85 kK
	19.9	$^4A_2(F) \rightarrow {^4A_2(P)}$	
$Ni(H_2O)L$	11.6	$^3B_1(F) \rightarrow {^3A_2(F)}$	$\alpha = 100°$
	13.6	$^3B_1(F) \rightarrow {^3B_2(F)}$	$D_q(ax) = D_q(eq)$
	16.0	$^3B_1(F) \rightarrow {^3E(F)}$	= 1.4 kK
	19.9	$^3B_1(F) \rightarrow {^1A_2(G)}$	
	22.2	$^3B_1(F) \rightarrow {^1E(D)}$	

TABLE III. Comparison of the E.S.R. Parameters of Some Vanado(IV)–Polyoxotungstic Complexes. R is defined as $g_\parallel/A_\parallel$.

Compound	$g_\parallel$	10^4 $A_\parallel$	R	Coordination	Reference
α_1-$VOP_2W_{17}O_{62}^{8-}$	1.885	−158	−119.3	6	16
α_2-$VOP_2W_{17}O_{62}^{8-}$	1.918	−160.5	−119.5	6	13
α-$VOSiW_{11}O_{39}^{6-}$	1.930	−164	−117.7	6	12
$VOW_5O_{18}^{4-}$	1.949	−167	−116.7	6	15
$VOAs_2W_{20}O_{69}^{8-}$	1.869	−175.5	−106.5	5	this work

P, As) [11, 12] or $VO(P_2W_{17}O_{61})^{n-}$ [13]. The $g_\perp$ and $A_\perp$ parameters have approximately the same values for all the complexes but $g_\parallel$ and $A_\parallel$ for VOL are weak: 1.87 and -175.5×10^{-4} cm^{-1} instead of about 1.92 and -165×10^{-4} cm^{-1} for the other complexes.

With the C_{4v} group symmetry, the ground state can be either $^2B_2$ or ^2E. The E.S.R. spectrum being easily observed at room temperature, we can assume that the ground state is not orbitally degenerated and that the unpaired electron lies in the b_2 molecular orbital which, in a LCAO–MO approach, could be expressed as

$$|b_2\rangle = a|d_{xy}\rangle + a'|\phi b_2\rangle$$

where ϕb_2 represents the ligand orbital combination having B_2 symmetry. According to [14], the excited states would be:

$$|e\rangle = b|d_{xz}, d_{yz}\rangle + b'|\phi_e\rangle$$

$$|b_1\rangle = c|d_{x^2-y^2}\rangle + c'|\phi b_1\rangle$$

$$|a_1\rangle = d|d_{z^2}\rangle + d'|\phi a_1\rangle$$

The ESR parameters describing a d_{xy} unpaired electron in a C_{4v} ligand field can be approximately expressed as [17, 18]:

$$g_\parallel = g_e - \frac{8a^2c^2\lambda}{\Delta E(B_1 \leftarrow B_2)}$$

$$g_\perp = g_e - \frac{2a^2b^2\lambda}{\Delta E(E \leftarrow B_2)}$$

$$A_\parallel = P[-\tfrac{4}{7}a^2 - K + (g_\parallel - g_e) + \tfrac{3}{7}(g_\perp - g_e)]$$

$$A_\perp = P[\tfrac{2}{7}a^2 - K + \tfrac{11}{14}(g_\perp - g_e)]$$

$g_e = 2.0023$ is the free electron g factor, λ corresponds to the free-ion spin–orbit coupling constant, K is the isotropic Fermi contact term and $P = g_e g_n \beta_e \beta_n \langle r^{-3} \rangle$. P and λ depend on the effective charge of the metal ion. Values corresponding to a VO^{2+} ion are usually taken in polyoxotungstic complexes [11, 12], $\lambda = 170$ cm^{-1} and $P = 0.0128$ cm^{-1}. a and K values can be calculated from the preceding equations. We have found a = 0.97 and K = 0.69. The a value shows that, in the ground state, the unpaired electron is almost completely located on the vanadium atom.

The electronic spectrum of VOL shows three absorption bands at 13.5, 19.0 and 22.7 kK. Intervalence charge transfer bands $V^{IV} \rightarrow W^{VI}$ are generally observed around 20–24 kK in this type of compound [11]. So, the 22.7 kK band can be attributed to $V^{IV} \rightarrow W^{VI}$ transfer. The two others are d–d transitions. We take the observed optical band at 13.5 kK to represent the $B_2 \rightarrow E$ transition. The third band, near the intervalence transfer and poorly resolved, can be assigned to the $B_2 \rightarrow B_1$ transition.

The values of *b* and *c* can then be obtained from the preceding equations. However, the calculated values appear to be greater than one, which is physically impossible. The adopted values of λ and P, corresponding to a VO^{2+} ion, are probably responsible for such an inconsistency. An increase of the effective charge on the vanadium atom could occur and then lead to an increase of λ.

The low $g_{\parallel}$ and $A_{\parallel}$ values can be correlated with the removal of an oxygen ligand in order to obtain pentacoordinated vanadium from hexacoordinated one. Within a family of compounds such as polyoxotungstates we suggest that the ratio $g_{\parallel}/A_{\parallel}$ could be a convenient empirical index related to the coordination geometry. This ratio shifts from about −120 cm to −107 cm when the coordination number decreases from six to five. Looking at Table III, we see that the only decrease of $g_{\parallel}$ has no real meaning.

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