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Organophosphorus Anion Coordination. Part V: Stabilization of Polymeric Pseudo-octahedral Complex Ions of Cobalt(II) and Nickel(II)

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Reaction of the β-ketophosphonate anion ligands $[(C_2H_5O)_2P(O)CHCOCH_2R]^-$ *(*$R = N(CH_3)_2$, L_a; $R = N(C_2H_5)_2$, L_b; $R=N(CH_2)_4O$ L_c; $R=N(CH_2)_5$, L_d*) with nickel and cobalt nitrates and perchlorates leads to new compounds of the type* $[Ni_7(OH)_6(L)_6](NO_3)_2$ *(*$L = L_a, L_b$*) and* $[M_7(OH)_6(L)_6](ClO_4)_2$ *(*$L = L_a, L_b, L_c, L_d$*). These compounds are characterized by elemental and crystallographic analyses and are shown to be 2–1 electrolytes in nitromethane solution. Magnetic and spectroscopic (i.r. and visible) data are reported and suggest a distorted octahedral structure.*

Introduction

The difference in the ability of nitrate and perchlorate groups to form coordination bonds is well established. For example, the tendency of NO_3^- to act as a ligand is manifest in the molecular complexes $[M(NO_3)_2(Ph_3PO)_2]$[1] whereas with ClO_4^- ionic derivatives of the type $[M(Ph_3PO)_4](ClO_4)_2$ are formed[2]. In order to study the influence of these functional groups, it appeared worthwile to examine reactions between the γ-amino β-ketophosphonates $(C_2H_5O)_2P(O)CH_2COCH_2R$ designated by LH (L_aH, $R = N(CH_3)_2$; L_bH, $R = N(C_2H_5)_2$; L_cH, $R = NCH_2CH_2OCH_2CH_2$; L_dH, $R = NCH_2CH_2CH_2CH_2CH_2$) and metal perchlorates and nitrates. Moreover, it is interesting to compare the chemical behaviour of our β-ketophosphonate group with another ligand of the type $(CH_3O)_2P(O)CH_2CON(CH_3)_2$ towards nickel(II) and cobalt(II) perchlorates. In fact, it has been suggested that the organic moiety in the $[M[(CH_3O)_2P(O)CH_2CON(CH_3)_2]_3](ClO_4)_2$ complexes acts as a chelating agent *via* the phosphoryl and carbonyl oxygen atoms[3].

Although the oxy-anion nitrate may be coordinated as in the $[M(NO_3)L]$ complexes[4], the compounds considered in this paper are of ionic type and correspond to the formula $[M_7(OH)_6(L)_6]X_2$ ($M^{2+} = Co^{2+}, Ni^{2+}$, $X^- = ClO_4^-$ for all ligands L^-; $M^{2+} = Ni^{2+}$, $X^- = NO_3^-$, $L^- = L_a^-, L_b^-$). This stoichiometry was established by analytical, crystallographic, conductimetric and IR spectroscopic techniques; supplementary data concerning the geometric arrangement about the metal atoms were obtained by magnetism and visible spectroscopy.

Experimental

The β-ketophosphonate ligands $(C_2H_5O)_2P(O)CH_2COCH_2R$ with $R = N(CH_3)_2$ (L_aH); $R = N(C_2H_5)_2$ (L_bH); $R = N(CH_2)_4O$ (L_cH) and $R = N(CH_2)_5$ (L_dH) were prepared by methods described previously[5].

Perchlorate complexes were obtained by adding the ligand (10^{-2} mol) to an acetone solution of the appropriate metal salt $M(ClO_4)_2 \cdot 6H_2O$ with $M^{2+} = Co^{2+}$, Ni^{2+} (5×10^{-3} mol). When LH is L_aH or L_bH, the presence of a slight excess of ligand is necessary to yield a microcrystalline product. In a few cases, the powdery solids formed could be recrystallized from xylene to give single crystals. Some of these products appeared to be solvated as evidenced by analytical data (IR bands due to xylene were masked by complex absorptions).

Whereas the L_aH ligand reacts with $[Ni(OH_2)_6](NO_3)_2$ in ethanol or acetone solutions to form the expected compound, with the L_bH ligand the use of acetone as solvent leads to a mixture of powdery $[Ni_7(OH)_6(L_b)_6](NO_3)_2$ and crystals of $[Ni(NO_3)L_b]$[6]. A pure product could be isolated from ethanol solutions in which were to stand for at least one day. The analysis of crystals which precipitated from a xylene solution containing the $[Ni_7(OH)_6(L_a)_6](NO_3)_2$ complex indicated the presence of 0.6 mol of solvent.

The deuterated complex was prepared by mixing an acetone solution of the metal salt (5×10^{-3} mol) with a 2:1 acetone – D_2O solution containing the ligand (10^{-2} mol).

All solids were filtered and washed with small amounts of solvent and diethyl ether and dried *in vacuo*. Physical measurements were carried out as previously reported[7].

Results

Analytical and Crystal Data

Carbon, hydrogen, nitrogen, phosphorus and nickel or cobalt analyses are reported in Table I for three of the complexes; with the L_a^- ligand, it was found that Ni/C = 1.16 and Ni/N = 1.17 when X^- is NO_3^- and respectively 1.20 and 0.88 for $X^- = ClO_4^-$. On the basis of these results, the stoichiometric formula requires:

(i) either 6 metallic atoms, 5 organic ligands and 7 nitrogen (*e.g.* 2 NO_3^-)

(ii) either 7 metallic atoms, 6 organic ligands and 8 nitrogen (*e.g.* 2 NO_3^-)

(iii) either 8 metallic atoms, 7 organic ligands and 9 nitrogen (*e.g.* 2 NO_3^-)

(iv) or 13 metallic atoms, 11 organic ligands and 15 nitrogen (*e.g.* 4 NO_3^-).

As will be shown later, the additional ions necessary for ionic stability are constitued by hydroxyl groups. The four possible formulations indicated above are given in Table I. Determinations of nitrate by the Dewarda technique and chloride analyses (Microanalysis Center of Thiais, FRANCE) were not reproductible with sufficient accuracy to permit definitive establishment of the formula. For this reason, it was desirable to determine the unit cell parameters for single crystals in order to obtain a value for the molecu-

TABLE I. Analytical Data.

Formula	%; d	% Exp (th)					d_{exp} (d_{th})
		C	H	N	P	M^{2+}	
$\{Ni_7(OH)_6(L_a)_6\}(NO_3)_2$	n = 0[a]	31.2 (31.57)	5.9 (5.88)	5.4 (5.45)	9.0 (9.04)	20.3 (20.01)	
	n = 0.6	33.3 (33.25)	6.0 (6.00)	5.4 (5.29)	8.9 (8.76)	19.6 (19.40)	1.50 (1.51)
$\{Ni_6(OH)_5(L_a)_5\}(NO_3)_2$	n = 0.6	(33.12)	(5.92)	(5.43)	(8.56)	(19.50)	(1.28)
$\{Ni_8(OH)_7La)_7\}(NO_3)_2$	n = 0.5	(33.26)	(6.04)	(5.21)	(8.95)	(19.41)	(1.72)
$\{Ni_{13}(OH)_{11}(L_a)_{11}\}(NO_3)_4$	n = 1.2	(33.24)	(5.96)	(5.35)	(8.67)	(19.45)	(1.39)
$\{Ni_7(OH)_6(L_a)_6\}(ClO_4)_2$	n = 0	30.2 (30.46)	5.6 (5.68)	3.9 (3.95)	8.7 (8.72)	19.1 (19.30)	1.56 (1.58)
$\{Ni_6(OH)_5(L_a)_5\}(ClO_4)_2$	n = 0	(29.74)	(5.55)	(3.85)	(8.50)	(19.38)	(1.35)
$\{Ni_8(OH)_7(L_a)_7\}(ClO_4)_2$	n = 0	(30.99)	(5.78)	(4.01)	(8.87)	(19.24)	(1.81)
$\{Ni_{13}(OH)_{11}(L_a)_{11}\}(ClO_4)_4$	n = 0	(30.13)	(5.62)	(3.90)	(8.62)	(19.34)	(1.47)
$\{Co_7(OH)_6(L_b)_6\}(ClO_4)_2$	n = 0	34.4 (34.48)	6.2 (6.31)	3.7 (3.65)	8.3 (8.07)	18.2 (17.94)	
	n = 1.2	37.4 (37.42)	6.5 (6.48)				1.44 (1.43)

[a] n designates the quantity of xylene.

TABLE II. X-ray Cristallographic Data of the Complexes $\{M_7(OH)_6(L)_6\}X_2 \cdot nC_2H_{10}$.

Data	M^{2+}; L^-; X^-; n	Ni^{2+}; L_a^-; NO_3^-; 0.6	Ni^{2+}; L_a^-; ClO_4^-; 0	Co^{2+}; L_b^-; ClO_4^-; 1.2
	a (Å)	14.12 ± 0.04	13.07 ± 0.08	29.30 ± 0.15
	b (Å)	25.45 ± 0.10	20.60 ± 0.10	23.40 ± 0.10
	c (Å)	13.10 ± 0.04	18.50 ± 0.15	17.05 ± 0.08
	α	91°20′ ± 20′	90°	90°
	β	96°20′ ± 20′	116°20′ ± 20′	105°50′ ± 10′
	γ	91°25′ ± 10′	90°	90°
	V(Å^3)	4670 ± 50	4470 ± 70	11250 ± 150
	d_{exp}	1.50 ± 0.05[a]	1.56 ± 0.05[b]	1.44 ± 0.05[c]
	Z	2	2	4
	d_{th}	1.51 ± 0.04	1.58 ± 0.03	1.43 ± 0.04
Reflections				
	h k l			h + k = 2n
	h 0 l		l = 2n	l = 2n (h = 2n)
	0 k 0		k = 2n	(k = 2n)
Group		PTor Pl	$P2_1/c$	Cc or C_2/c
Symmetry		t	Monoclinic	Monoclinic

[a] The density is measured by flotation in a mixture of cyclohexane–bromoform. [b] The density is measured by pycnometry in cyclohexane. [c] The density is measured by flotation in a mixture cyclohexane–carbon tetrachloride.

lar weight by indirect means (see Table II). Discrepancy between theoretical and experimental densities observed in the case of the two stoichiometries $[Ni_6(OH)_5(L)_5]X_2$ and $[Ni_8(OH)_7(L)_7]X_2$ suggested the choice of the formula $[Ni_7(OH)_6(L)_6]X_2$. With a greater estimated error in density, the formula $[Ni_{13}(OH)_{11}(L)_{11}]X_4$ cannot be ruled out. However, barring a highly improbable statistic disorder, the crystallographic requirement that one of the thirteen metal atoms in the space groups $P2_1/c$ occupies a one-fold position (density measurements yielded a value of approximately one molecule per unit cell) is not compatible with the existence of such a structure. The formula $[M_7(OH)_6(L)_6]X_2$ was therefore postulated for all our complexes.

Conductimetric and IR Spectroscopic Data

On the basis of the molecular weight deduced from the previous result, it is found that the compounds behave as 2–1 electrolytes in nitromethane solution. Equivalent conductances are 175–195 Ω^{-1} cm^2 mol^{-1} at $8.5 \times 10^{-4} M$ (the values expected for 2×10^{-4} to $2 \times 10^{-3} M$ solutions lie in the range 160–200 Ω^{-1} cm^2 mol^{-1}[8]).

The vibrational spectra of two compounds are listed Table III. As found previously[7,9], the β-ketophosphonates coordinate at least through both oxygen atoms, as shown by the observed decrease in the $\nu(C=O)$ and $\nu(P=O)$ stretching frequencies. There is no evidence that the metal ion is bonded with the nitrogen atom of the organic moiety.

Whatever the nature of X^-, no interaction with the metal ion was detected. The number and positions of the bands attribuable to the nitrate group suggest that the latter is ionic in its D_{3h} symmetry. If coordination occured, ν_1 would become active and the degeneracy of the ν_3 and ν_4 (E′) would be lifted[10]. The presence of a single band assigned to the combination mode $\nu_1 + \nu_4$ is also consistent with this conclusion[11]. Similarly, no splitting of the broad strong band at about 1100 cm^{-1} indicative of a monodentate (C_{3v}) or a bidentate (C_{2v}) coordinating agent appears in perchlorate complexes[12]. These results are compatible with the observation that the far infrared spectra in the range 450–200 cm^{-1} are identical for all complexes of the type $[Ni_7(OH)_6(L)_6]X_2$ containing a given ligand L^-; accordingly no Ni–X bonds are present. Analogous behaviour of X^- in the cobalt compounds may also be assumed since the X-ray powder patterns suggested that the cobalt and nickel complexes with the L_a^-, L_b^- and L_d^- ligands were isomorphous (the complex containing L_c^- was poorly crystallized).

A very sharp peak at 3645 cm^{-1} in the perchlorate compounds and a broader one at 3580 cm^{-1} in the nitrate complexes were attributed to the stretching mode of the OH groups[13]; this assignment is further supported by the fact that no band characteristic of the bending mode of the water molecule appears in the 1600 cm^{-1} region. Since the requirements of the anionic contribution in the complexes are fulfilled by the two X^- ions, it is considered that the six OH^- groups are involved in bond formation. In an attempt to obtain further information on the interaction of the hydroxyl ions with the metals, we used the deuteration technique for the complex $[Ni_7(OH)_6(L_d)_6](ClO_4)_2$. Unfortunately, the presence of the two $\nu(OH)$ and $\nu(OD)$ bands in the spectrum (see Table III) showed that isotopic substitution of OH^- was incomplete. The band at 509 cm^{-1} decreases in intensity and lies in a range which permits tentative assignment to Ni–OH stretching (563–500 cm^{-1}[14]); the additionnal band at 494 cm^{-1} can be possibly attributed to the ν(Ni–OD) mode since the observed frequency shift and the value 1.03 for the ration ν(Ni–OH)/ν(Ni–OD) agree well with the expected isotopic effect[15].

It appears that the shape and the position of the band due to $\nu(OH)$ depend on the nature of X^-. In contrast to the perchlorate complexes, the corresponding band in the nitrate derivatives is characterized by a broadening and a shift of 50 cm^{-1} towards lower frequencies. These two features indicate the existence of hydrogen bonds[16]; such bonding could possibly occur between the complex cation *via* the hydroxyl groups and the NO_3^- anion. The observed asymmetry of the band

TABLE III. Ir Spectra of $\{Ni_7(OH)_6(L)_6\}X_2$ (cm^{-1}).

L^-, X^-, OH^- Compound	L^- $\nu(P\rightarrow O)$; ω(cycle); $\nu(C{=}O)$ and/or $\nu_{as}(P{=}C{=}C)$	X^- NO_3^{-a} and ClO_4^{-b}	OH^- $\nu(OH)$, $\nu(OD)$; ν(Ni–OH), ν(Ni–OD)
$\{Ni_7(OH)_6(L_b)_6\}(NO_3)_2$	1180; 1420; 1584(ep), 1572 ($\Delta\nu = 78$)	837(ν_2), 1366(ν_3), 1738 ($\nu_1 + \nu_4$)	3580*
$\{Ni_7(OD)_x(OH)_{6-x}(L_d)_6\}(ClO_4)_2$	1180; 1415; 1584(ep), 1570 ($\Delta\nu = 75$)	~1100*(ν_3), 624(ν_4)	3645, 2685; 509, 494

* Broad absorption.

[a] $\nu_1 : \nu_s(N–O)\ (A_1')$; $\nu_2 : \pi(NO_3)(A''_2)$; $\nu_3 : \nu_d(N–O)(E')$; $\nu_4 : \delta_d(ONO)(E')$. [b] $\nu_1 : \nu_s(Cl–O)\ (A_1)$; $\nu_2 : \delta_d(ONO)(E)$; $\nu_3 : \nu_d(Cl–O)\ (F_2)$; $\nu_4 : \delta_d(O–Cl–O)\ (F_2)$.

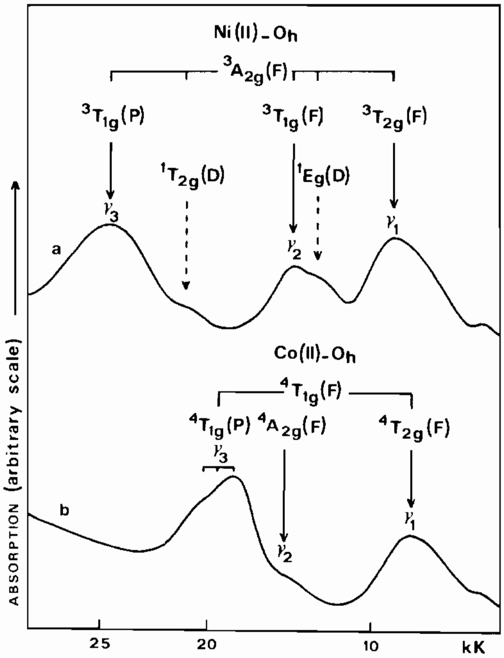

Figure 1. Diffuse reflectance spectra; a) $[Ni_7(OH)_6(L_a)_6](ClO_4)_2$, b) $[Co_7(OH)_6(L_a)_6](ClO_4)_2$.

characteristic of this ν(OH) mode in the perchlorate complexes suggests that such interactions may also exist but they would appear to be very weak in view of the observed frequency[17] and of the value $\nu(OH)/\nu(OD) = 1.36$[16]. This tendency to form hydrogen bonds with the hydroxyl groups is compatible with the sequence established by Kecki for the H_2O molecule, *i.e.* $I^- > Br^- > Cl^- > NO_3^- > F^- > ClO_4^-$ [18].

Magnetic and Electronic Spectra

The magnetic moments measured at room temperature were 3.20–3.25 B.M. for the green nickel complexes and 4.75–5.00 B.M. for the pink cobalt ones. These values are typical for octahedrally coordinated nickel(II) (3.0–3.3 B.M.) and cobalt(II) (4.7–5.2 B.M.)[19].

The number, intensities and general shape of the bands of the visible spectra (Figure 1) also suggest an octahedral configuration[20]. Moreover, this structure is retained in chloroform solution. All the $[Ni_7(OH)_6(L)_6]X_2$ complexes with a given L^- (L_a^- or L_b^-) exhibit identical electronic patterns; this is in agreement with our previous conclusion concerning the unique nature of the complex cation irrespective of the choice of anions. Small differences in position observed for each L^- ligand in the cobalt or nickel complexes are attributed to a specific ligand field. Assignments of the electronic transitions are made by using the semi-empirical diagrams of energy levels established by Reedjik[21,22].

The relatively high value obtained for the molar extinction coefficients (ε_{max} of about 100 to 180 $cm^2\ mol^{-1}$) may be interpreted as a deviation from regular octahedral symmetry.

Discussion

It was expected that the X-ray crystallographic study of the $[Ni_7(OH)_6(L_a)_6](ClO_4)_2$ complex would provide more definite structural information not otherwise available from the foregoing data. Preliminary results[23] were obtained by using the multisolution method with the programm MULTAN[24]; they reveal a centrosymmetric arrangement in the $P2_1/c$ unit cell with one nickel atom lying in the center of symmetry and six other metal atoms in a general position. In the complex cation, each nickel atom has a distorted octahedral environment in which 24 donor atoms (oxygen and nitrogen are indistinguishable) are coordinated to seven nickel atoms. The structure is thus built up by seven octahedra with shared edges; such a scheme is well known in the case of the isopolyanion $[Mo_7O_{24}]^{6-}$ [25]. Since there are 24 donor atoms and in order to satisfy a six-coordination number for each metal in the $[M_7(OH)_6(L)_6]^{2-}$ complex anion, the organic ligand is supposed to be tridentate. Several difference Fourier maps were used in an attempt to locate the remaining atoms but the complete structure could not be solved, presumably because of the imperfection of the studied crystal and maybe also of the high temperature factors. At this stage of the study, another crystallisation method should be set up. These results, however, are already confirming the proposed stoichiometry.

The fact that ionic complexes with the perchlorate anions were always isolated is compatible with the weak coordinating ability of this group. On the other hand, the nitrate anion behaved preferentially as a ligand and the formation of the molecular complexes $[M(NO_3)L]$ was generally favoured.

Moreover, the particular stoichiometry of the complexes with the two β-ketophosphonates $(C_2H_5O)_2P(O)CH_2COCH_2N(CH_3)_2$ and $(CH_3O)_2P(O)CH_2CON(CH_3)_2$ reflects the importance of the methylene group between the carbonyl and the amino group in establishing different chemical behaviour towards the metal perchlorates. The organic moiety in our complexes is ionic and probably tridentate whereas in the compounds studied by Good is neutral and bidentate[3].

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