Interaction of Aminooxyalkylphosphonic Acids with Cobalt(II), Nickel(II), and Copper(II)

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The series of new complexes with perchlorate cobalt(II), nickel(II), copper(II), and aminooxyalkylphosphonic acids have been synthesized in polycrystalline form. They are first synthesized complexes with aminooxyalkylphosphonic acids. The structures were proposed based on spectroscopic data (IR, UV VIS, FIR, EPR) and the measured magnetic moments. The oxygen atom of the aminooxy group takes part in coordination with metal ion in aminooxymethylphosphonic acid but it does not coordinate in 1-aminooxyethylphosphonic acid and 2-aminooxyethylphosphonic acid. The weaker binding ability of the aminooxy group oxygen atom could be attributed to geometry of the ligands.

Aminooxyalkylphosphonic acids may be considered as the phosphonic analogues *II* of aminooxyalkylcarboxylic acids *I* in which —COOH group is replaced by —PO_3H_2 group.

$H_2NORCOOH$	$H_2NORPO(OH)_2$
I	*II*

where R = CH_2 (*a*); CH_3CH (*b*); and CH_2CH_2 (*c*).

While interactions of *I* with transition metals have been studied in solution [1—3] and in the solid state [4—6], complexes of *II* have not been investigated yet. The introduction of the oxygen atom between nitrogen and carbon atom in given compounds seems to reduce the coordinating ability of the nitrogen lone pair when compared with the corresponding aminoalkylcarboxylic or aminoalkylphosphonic acids. Anyway, the coordination ability of the nitrogen atom of the same aminooxycarboxylic acids and their esters towards transition metals has been established [6]. The aminooxycarboxylic acids act as negatively charged chelating ligands and form neutral complexes with Cu(II) and Ni(II) coordinating *via* the nitrogen atom and carboxylic oxygen atom. The Co(II) with some of aminooxycarboxylic esters bounds only *via* nitrogen atoms and chloride ions. Carboxylic group does not participate in binding in this case [6].

Compounds *II* are also interesting as potential polydentate ligands possessing five donor atoms: nitrogen and oxygen atom from aminooxy group and three oxygens from phosphonyl group. Complexes with these ligands are unknown up to now.

Recently, several compounds *II* have been obtained [7, 8] and three of them have been found to be slow binding inhibitors of aspartate and alanine aminotransferases [8].

The aim of the present paper was to prepare compounds of Co(II), Ni(II), and Cu(II) with the following ligands: aminooxymethylphosphonic acid (*IIa*), 1-aminooxyethylphosphonic acid (*IIb*), and 2-aminooxyethylphosphonic acid (*IIc*), and determination of their structures by spectroscopic and magnetic methods. Some complexes have been obtained in the solid state and their preliminary results were reported earlier [9].

EXPERIMENTAL

All reagents used in the synthesis were obtained from Fluka. Ligands: *IIa, IIb,* and *IIc* were synthesized according to the reported procedures [8] and characterized by analytical and spectral methods (IR, ^{1}H NMR) before they were used for complexation.

The stoichiometry of the crystals was established based on microanalyses (P, N, H) and Co, Ni, Cu by atomic absorption spectrophotometer (ASA) on Perkin—Elmer 1100 which gave satisfactory results.

Infrared absorption spectra were obtained in KBr pellets with a Perkin—Elmer FTIR 1600 spectrophotometer in the range 400—4000 cm^{-1}. Low frequency

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spectra (100—600 cm^{-1}) in nujol mulls on polyethylene plates were obtained on a Perkin—Elmer System FTIR 2000 spectrophotometer.

Diffuse reflectance spectra were measured in the $\tilde{\nu}$ range 12 500—48 000 cm^{-1} with a Hitachi 365 UV VIS spectrophotometer interfaced to an IBM PC/XT/AT computer.

The acidity constants have been determined by potentiometric titrations in aqueous solution at 298 K and $I(\text{KNO}_3) = 0.1$ M. The 691 pH-meter (Metrohm) was calibrated against two standard buffer solutions covering the pH range 4—8 using universal electrode.

Magnetic susceptibility measurements (80—300 K) were carried out using the Gouy method on a sensitive Cahn RM-2 electronic balance at a magnetic field strength 788 kA m^{-1}. The calibrant employed was HgCo(NCS)_4 for which the magnetic susceptibility χ_g was taken as 16.44×10^{-6} cm^3 g^{-1}. Corrections for diamagnetism of the constituent atoms were made by Pascal constants [10]. The effective magnetic moments were calculated from the equation $\mu_\text{eff} = 2.83[\chi_M^\text{corr}(T - \Theta)]^{1/2}$.

The EPR powder spectra were recorded on a EPR-SE-X/25 A/B spectrometer at X-band frequency (9.5 GHz) at 293 K and 78 K using DPPH as internal standard.

Complexes *IIIa*—*Vc* in polycrystalline form were obtained by mixing the concentrated aqueous solution of cobalt(II), nickel(II), or copper(II) perchlorate hexahydrate and disodium salts of *IIa* or *IIb* in the 1 : 1 mole ratio. Only copper(II) complex with disodium salts of *IIc* could be prepared. Final pH value of the solutions was between 6.5—8.0. The complexes which precipitated out immediately were filtered off, washed with warm water and dried in open air. They were stable under normal laboratory conditions over a long period of time. Complexes were insoluble in nonpolar and polar solvents, which suggests their polymeric structure.

RESULTS AND DISCUSSION

The ligands were characterized potentiometrically, the experimental dissociation constants measured for aminooxyalkylphosphonic acids are summarized in Table 1. For comparison, some data for aminoalkylphosphonic acids are included [7, 11, 12]. The acidity constants of the phosphonic group of aminoalkylphosphonic acids are slightly larger than those of the related aminooxyalkylphosphonic acids. On the other hand, the basicity of aminooxy group is markedly lower when compared with basicity of the amino group of the analogous aminoalkylphosphonic acids. It decreases in the order *IIc, IIb, IIa*. The same trend was observed in a series of 2-aminoalkylcarboxylic and 2-aminooxyalkylcarboxylic acids but absolute differences between the dissociation constants values in the last case were greater [3]. The decreased basicity of NH_2OCHR is explained by the electron-withdrawing properties of the oxygen atom of NH_2O group.

The prepared complexes, their denotation, and elemental analysis are given in Table 2, eletronic absorption, IR and EPR spectra, as well as magnetic data are given in Tables 3 and 4.

In the visible absorption region of *IIIa*, a multiple structured absorption band was found in the range 16 300—18 500 cm^{-1} corresponding to the transition $^4T_{1\text{g}}(\text{F}) \rightarrow {}^4T_{1\text{g}}(\text{P})$ [13]. The shoulder appears on the high-energy side at 21 120 cm^{-1}. Additional absorption band appears at about 12 500 cm^{-1}, which might suggest a coordination number five [14]. Magnetic moment value (4.66 μ_B) supports this conclusion [15]. According to the position and the shape of the asymmetric bands it could be assumed that coordination sphere of cobalt ion is an intermediate between square pyramidal and trigonal bipyramidal [16].

The diffusion reflectance spectrum of *IVa* is characteristic of six-coordinated, pseudooctahedral structure [13, 17]. The bands at 24 200 cm^{-1} and 13 340 cm^{-1} correspond to $^3A_{2\text{g}} \rightarrow {}^3T_{1\text{g}}(\text{P})$ and $^3A_{2\text{g}} \rightarrow {}^3T_{1\text{g}}(\text{F})$ transition, respectively. A band splitting due to O_h symmetry lowering was observed at 15 160 cm^{-1} which apparently corresponds to the spin-forbidden transition $^3A_{2\text{g}} \rightarrow {}^1E_\text{g}$. The magnetic moment (2.90 μ_B) is somewhat lower than those normally encountered in octahedral complexes of nickel(II) and might suggest weak antiferromagnetic interaction between nickel(II) atoms [17, 18].

The *d*—*d* transition of Cu(II) complexes is marked-

Table 1. Dissociation Constants of the Aminoalkylphosphonic and Aminooxyalkylphosphonic Acids

Compound	p*K*a$_2$	p*K*a$_3$	p*K*a$_3$	Ref.
	PO_3H_2	ONH_2	NH_2	
$\text{NH}_2\text{CH}_2\text{PO}_3\text{H}_2$	5.42		10.08	[11]
$\text{NH}_2\text{OCH}_2\text{PO}_3\text{H}_2$	4.29	6.86		[7]
$\text{NH}_2\text{CH(CH}_3\text{)PO}_3\text{H}_2$	5.55		10.11	[12]
$\text{NH}_2\text{OCH(CH}_3\text{)PO}_3\text{H}_2$	4.45	7.35		This paper
$\text{NH}_2\text{CH}_2\text{CH}_2\text{PO}_3\text{H}_2$	6.21		10.92	[12]
$\text{NH}_2\text{OCH}_2\text{CH}_2\text{PO}_3\text{H}_2$	4.80	7.45		This paper

Table 2. Analytical Data for the Complexes

Complex	w_i(calc.)/% w_i(found)/%			
	P	N	H	Me
Co[(*IIa*)(H_2O)$_2$] · 0.5H_2O, *IIIa*	13.52	6.11	3.96	25.72
	13.74	6.21	4.14	25.95
Co[(*IIb*)(OH)(H_2O)$_3$] · 0.5H_2O, *IIIb*	11.10	5.01	5.41	21.12
	11.43	4.70	5.48	20.90
Ni[(*IIa*)(H_2O)$_3$], *IVa*	13.03	5.89	4.24	24.68
	13.03	5.56	4.07	24.57
Ni[(*IIb*)(H_2O)$_3$], *IVb*	12.30	5.56	4.80	23.31
	12.98	5.50	4.74	23.12
Cu[(*IIa*)(H_2O)$_2$], *Va*	14.04	6.35	3.65	28.80
	14.29	6.10	3.59	29.01
Cu[(*IIb*)(OH)(H_2O)] · 2H_2O, *Vb*	11.27	5.09	5.14	23.13
	11.37	4.59	4.96	23.33
Cu[*IIc*], *Vc*	15.29	6.91	2.98	31.37
	15.46	6.90	3.23	31.02

Table 3. Diffuse Reflectance Spectral Data and Magnetic Moments

Complex	Colour	$\tilde{\nu} \cdot 10^{-3}/\text{cm}^{-1}$	$\dfrac{\mu_{\text{eff}}}{\text{B.M.}}$
IIIa	Dark violet	12.50; 16.31; 17.54; 18.45; 21.12	4.66
IVa	Green	13.34; 15.16; 24.20	2.90
Va	Blue	13.98; 14.79	–
IIIb	Bright violet	15.48; 16.13; 16.67; 17.39; 19.42	4.78
IVb	Green	13.69; 15.33; 25.00	2.99
Vb	Blue	13.33	–
Vc	Blue	12.50	–

Table 4. Characteristic Infrared Wavenumbers ($\tilde{\nu}/\text{cm}^{-1}$) of Selected Aminoalkylphosphonic Acids and their Complexes. IR Spectral Assignments of Diagnostic Band in 100—4000 cm^{-1} Region

IIa	*IIIa*	*IVa*	*Va*	*IIb*	*IIIb*	*IVb*	*Vb*	*IIc*	*Vc*	Assignment
	1654	1650	1633		1647	1647	1639			$\delta_{\text{sc}}(H_2O)$
	1604	1600	1589		1583	1584	1580		1585	$\delta(NH_2)$
1445	1409	1411	1435					1418	1400	$\delta_{\text{sc}}(CH_2)$
								1391		
1359	1333	1328	1317					1320	1321	$\rho_{\text{w}}(CH_2)$
				1459	1450	1459	1453			$\delta_{\text{as}}(CH_3)$
				1380	1381	1371	1378			$\delta_{\text{s}}(CH_3)$
1286	1247	1247	1255	1297	1298	1299	1298	1301	1309	$\nu(CO)$
1128	1091	1100	1092	1175	1105	1101	1107	1113	1095	$\nu_{\text{d}}(PO_3)$
1056	1044	1044	1044	1071	1072	1059	1075	1074	1071	
1018	1015	1018	1018	1045	1048	1022	1051		1024	
				1132	1132	1135	1131			$\rho_{\text{r}}(CH_3)$
947	967	972	974	925	988	962	987	923	982	$\nu_{\text{s}}(PO_3)$
920										
	434	444	442		431	445	441			$\nu(MO_{\text{water}})$
	294	300	304		281	305			307	$\delta(OMO)$
					438	263	266		268	$\nu(MN)$
					268					
					196					$\delta(NMN)$

Abbreviations: ν – stretching; δ – in-plane bending; δ_{sc} – scissoring; ρ_{w} – wagging; ρ_{r} – rocking. Subscripts s, as, and d denote symmetric, antisymmetric, and degenerate modes, respectively.

ly red-shifted from the visible region spectrum into the near IR, indicating that the ligand environment of Cu in that site is either a distorted tetrahedral, tetragonal or five-coordinated trigonal bipyramidal structure [19]. On the other hand, the EPR spectrum of *Va* shows absorption at 293 K in the field region corresponding to $\Delta M_\mathrm{s} = 1$ and $\Delta M_\mathrm{s} = 2$ transition of $g_1 = 2.159$ and $g_2 = 5.122$, respectively. Significant effect of temperature is observed in the EPR spectrum at 78 K. The absorption coming from dimeric species disappears and only broad isotropic band is observed ($g_1 = 2.183$). On the other hand, the electronic absorption broad band with maximum at 12 980 cm^{-1} and a shoulder at the higher energy (14 790 cm^{-1}) may be still a support of an elongated tetragonal structure [20, 21]. The bands observed are tentatively assigned to $^2B_{1\mathrm{g}} \rightarrow {}^2E_\mathrm{g}$ and $^2B_{1\mathrm{g}} \rightarrow {}^2A_{1\mathrm{g}}$ transition, respectively. A polymeric chain structure with tetragonally distorted environment is therefore suggested in which coordination number six is retained around the metal ion. The polymeric arrangement has influence on the EPR spectrum due to the magnetic interaction between the copper centres or the misalignment of the magnetic axes along the chain [22]. Additionally a shoulder on the lower-energy side (below $\tilde{\nu} =$ 12 500 cm^{-1}) might suggest a five-coordinated trigonal bipyramidal structure. It corresponds to dimeric structure, as suggested by the EPR spectrum at 293 K.

The presence of oxygen between nitrogen and carbon atoms lowers the basicity of the amino group towards protons (Table 1) and decreases the coordinating ability of the amino group towards the metal ion. The $\mathrm{NH_2}$ stretching region shows very broad poorly resolved absorption typical for strongly hydrogen-bonded —$\mathrm{NH_2}$ groups, so an assignment of the $\nu(\mathrm{NH_2})$ frequencies was impossible. The lack of a significant shift of the amino bending frequencies implies that the amino group is not coordinated (Table 4). The coordination of the $\mathrm{PO_3}$ group is evident from its infrared spectrum (the negative shift to lower frequencies), but not all phosphono groups are involved in complex formation (Table 4). Unfortunately, we were not able to assign metal-oxygen stretching frequencies of the coordinated phosphonyl group, because of their low intensity [23]. Indirect evidence that the oxygen atom of aminooxy group is involved in the coordination is the fact that the deformation vibrations of the —$\mathrm{CH_2}$ group differ appreciably from those of the uncomplexed ligands. Coordination to metal ion also shifts the stretching vibration of the aminooxy CO group of 39 cm^{-1}, 39 cm^{-1}, 31 cm^{-1} to lower energies for the series *IIIa*, *IVa*, *Va*, respectively (Table 4). It indicates that the strength of the Cu—$\mathrm{ONH_2}$ bond becomes smaller. The Cu^{2+} ion in general likely favours amino group for coordination [11], but in this case it does not take place. New band which appeared at about 600 cm^{-1} may be assigned to the ring deformation [24].

Therefore it seems likely that the aminooxymethylphosphonic acid acts in a bidentate manner through the oxygen atoms from phosphonic and aminooxy groups forming complexes involving five-membered chelate ring. Additionally, the next oxygen atom from phosphonic group forms a bridge between metal atoms, which results in obtaining infinite polymeric chain. According to the position and the shape of the bands of diffusion reflectance spectrum nickel is six-coordinated, cobalt five-coordinated. This coordination is achieved by complexing with the water molecules (Table 4). Based on the EPR spectra analysis of *Va* exhibits more complicated polymeric structure. Dominating structure is such when two five-membered chelate rings connected together by Cu—O—Cu bridges form dimer species in which the coordination number of Cu(II) ion is five. Besides that another species are also observed. One can see the dimer species linked by Cu—O—P—O—Cu double bridge, which results in forming six-coordinated polymeric chain. The expected coordination number is completed by water molecules (Table 4). This Cu—O—P—O—Cu bridge is broken at higher temperature and dimeric structure prevails.

The compound *IIIb* has reflectance spectrum with multiple absorption bands near 18 000 cm^{-1} and 16 000 cm^{-1}, which is typical for both tetragonally and tetrahedrally distorted cobalt atoms coordination sphere. The assignment of the bands around 18 000 cm^{-1} is not easy because of their poor resolution due to the interaction between $^4A_{2\mathrm{g}}(\mathrm{F})$ and $^4T_{1\mathrm{g}}(\mathrm{P})$ states. The multiple bands between 17 400 cm^{-1} and 19 400 cm^{-1} are assigned to the transition $^4T_{1\mathrm{g}}(\mathrm{P}) \rightarrow ({}^4E_\mathrm{g}, {}^4A_{2\mathrm{g}})$. The bands between 16 000 cm^{-1} and 17 500 cm^{-1} may be attributed to the $^4A_2 \rightarrow {}^4T_1(\mathrm{P})$ transition and suggest the tetrahedral configuration. The value of the magnetic moment 4.78 μ_B is the borderline between the tetrahedral and octahedral regions for Co(II), while the electronic spectrum is typical for a coexistence of both pseudotetrahedral and high-spin octahedral units in the solid state and confirms this suggestion [13, 25].

In the diffusion spectrum of the *IVb* complex two absorption bands at 25 000 cm^{-1} and 13 690 cm^{-1} may be assigned to $^3T_{1\mathrm{g}}(\mathrm{P})$ and $^3T_{1\mathrm{g}}(\mathrm{F})$ transition, respectively and spin-forbidden transition $^3A_{2\mathrm{g}} \rightarrow {}^1E_\mathrm{g}$ (15 330 cm^{-1}) [17] indicating a pseudooctahedral geometry as evidenced by its magnetic moment (2.99 μ_B). The lower values of the magnetic moment are probably due to greater axial distortion and polymeric octahedral structure formation. The *d*—*d* absorption maxima in the spectra of *Vb* and *Vc* complexes allow assumption of the structure with coordination number five. The compounds *Vb* and *Vc* exhibit single, very broad bands with the maximum at 13 300 cm^{-1} and 12 500 cm^{-1}, respectively. These spectra are similar to those of imidazoline complexes [26] and may support the trigonal bipyramidal structure. Unfortunately, the copper polycrystalline complexes *Vb* and *Vc* do not exhibit any EPR spectrum at 293 K. It should be the result of the interactions between Cu(II) ions bridged in the case of the studied compounds through oxygen atom of hydroxy group (*Vb*) or oxygen atoms of phosphonic group (*Vc*). The oxygen atoms of these groups exhibit high ability to bind the neighbouring Cu(II) ions. This results in formation of polymeric structure complexes. Dynamic effect should be considered at 78 K since the temperature effect is seen on EPR spectrum as a broad isotropic band.

A lack of significant shift either of the CO stretching frequencies or of the adjacent methyl group in the obtained complexes when compared with the free ligand frequencies implies that the oxygen from aminooxy group is not coordinated. Nitrogen coordination comes from M—N stretching frequencies which appear in far infrared region (Table 4). New bands at 268 cm^{-1}, 263 cm^{-1}, and 266 cm^{-1} are tentatively due to formation of Co(II)—N, Ni(II)—N, and Cu(II)—N bonds, respectively. The analysis of the stretching vibrations (Table 4) suggests the bidentate coordination of the phosphonate ion in the nickel complex and unidentate in the cobalt and copper complexes.

The presence of water molecules in complexes is indicated by a broad band between 3300 cm^{-1} and 3550 cm^{-1} and weaker band around 1640 cm^{-1} which could be assigned to OH stretching and HOH bending vibrations, respectively [27, 28]. From the IR spectra it is evident that the water molecules in the polymeric crystals are involved in hydrogen bonding. This is indicated by broad bands around 3450 cm^{-1}. The coordination number six for nickel is achieved by coordination water molecules as ligand. It is confirmed by ν(Ni—O) stretching vibration which appears at 445 cm^{-1}. Additionally, for *Vb* and *IIIb* at 3390 cm^{-1} and 3319 cm^{-1}, respectively, a shoulder appears on water band. According to Refs. [28—31] this can be assigned to the OH stretch in the bridging OH group. The lack of any resonance transition in triplet state levels of the EPR spectrum at 293 K confirms interaction between neighbouring Cu(II) ions [22]. The coordination number five for *Vb* is completed by additional coordination water molecules as ligand. The band of 441 cm^{-1} is attributed to ν(Cu—O) stretching vibration. On the other hand, *IIIb* complex exhibits magnetic moment 4.78 μ_B which excludes the possibility of spin-spin interaction between the cobalt(II) centres. This indicates that the hydroxy group coordinates as a monodentate ligand. The presence of the new bands of Co(II)—N at 438 cm^{-1} and 268 cm^{-1} confirms coexistence of the tetrahedral and octahedral units in the solid state, respectively, as earlier suggested from the electronic spectrum. Additionally, the band at 196 cm^{-1} responsible for δ(N—Co—N) vibration supports the suggestion of tetrahedral surrounding around the cobalt atom [28]. So, mixed complex containing high-spin distorted tetrahedral units with CoN_2O_2 chromophore and high-spin tetragonally distorted octahedral units with CoO_6 chromophore is proposed. The required coordination number is completed by additional coordination hydroxy group and water molecules as ligand. Appearance of the band at 431 cm^{-1} confirms it.

The presence of the methyl group in one position results in the formation of the compounds containing polymeric complexes in which both ends of the ligands coordinate to different metal ions. The different behaviour of the aminooxymethylphosphonic acid from that of the aminooxyethylphosphonic acid probably can be explained by the steric hindrance of the CH_3 group and additionally a slightly more basic aminooxy group. The presence of the methyl group hinders the formation of the chelate ring by O atoms (from aminooxy group and phosphonic group). Since basicity of aminooxy group in all studied complexes differs inconsiderably, this would suggest that steric factors are more dominant than the electron-donating power of the aminooxy group nitrogen atom to oxygen atom.

Three oxygens of the phosphonic group (*Vc*) are bonded to copper atoms (Table 4). Bands at 3250 cm^{-1}, 3202 cm^{-1}, and 3130 cm^{-1} must be due to NH stretching vibrations of the amino group coordinated to the copper. The oxygen atom from aminooxy group does not take part in coordination. The weaker binding ability of *Vc* compared to *Va* could also be attributed to different structures of the ligands. The increasing length of the methylene chain joining the aminooxy and phosphonic groups causes different metal ion coordination. The coordination of five is achieved by chelation of a metal by phosphonic group while at the same time the two chelating oxygen atoms bind additionally to adjacent metal atoms. The fifth coordination site is occupied by the nitrogen atom from amino group. The 268 cm^{-1} band has been assigned to ν(Cu—N) vibration. This is supported by the presence of a similar band, near 300 cm^{-1} in numerous compounds containing the NH_2 donor group [24, 28]. Four bands at 307 cm^{-1}, 278 cm^{-1}, 205 cm^{-1}, and 192 cm^{-1} can be tentatively assigned as $\text{Cu}\cdots\text{O}$ stretching frequencies because phosphonyl group easily enters into $\text{Cu}\cdots\text{O}$ bonding. On the other hand, EPR spectra examination confirms the exchange interactions between Cu(II) ions. From the IR spectra it is evident that the water molecules are absent in the crystal [28].

The study of the molecular arrangement around the metals ions with similar ligands will be continued. Attempts are being made to grow single crystals suitable for X-ray crystallographic determination.

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