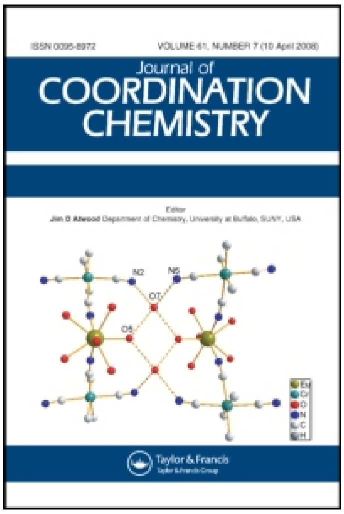

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Copper(ii), Nickel(II) and Cobalt(II) Complexes of 2-Aminooxy Acids and Their Esters

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COPPER(II), NICKEL(II) AND COBALT(II) COMPLEXES OF 2-AMINOOXY ACIDS AND THEIR ESTERS

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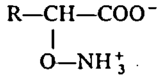
The donor properties of 2-aminooxy acids of general formula



$$\begin{array}{l} \mathrm{R{-}CH{-}COO^-} \\ \qquad | \\ \qquad \mathrm{O{-}NH_3^+} \end{array}$$

where R is H, CH_3, C_3H_7, $CH_3CH(CH_3)CH_2$ or $C_6H_5CH_2$, were investigated. Copper(II) and nickel(II) complexes with the ligands as well as cobalt(II) complexes with some of their esters were prepared. The compounds have been characterized spectroscopically. Esr. spectra of copper(II) complexes were also recorded. The 2-aminooxy acids behave as anionic ligands and form neutral complexes with Cu(II) and Ni(II) in which the central atoms are coordinated *via* the nitrogen atom of the ONH_2 group and one of the oxygen atoms of the carboxylate group. In the anhydrous complexes the other oxygen atom of the COO^- group acts as a bridging agent. Cobalt(II) forms a pseudotetrahedral structure which is completed by nitrogen atoms of two ONH_2 groups and two chloride ions.

Keywords: Aminooxy acids, copper(II), cobalt(II), nickel(II), complexes, sythesis

INTRODUCTION

The first 2-aminooxycarboxylic acid was synthesized as early as the end of the last century.[2] More attention, however, has been devoted to these compounds since their isolation from the natural sources canavanine and canaline.[3] After confirmation that the antibiotic cycloserine also belongs to this group, investigations were focused on the biological activity of aminooxy acids and their derivatives.[4–10]

Further bioactivity studies of these compounds reveal that some of them effect production of some hormones[11] and possess neurotropic properties.[12–14] Numerous reports have been published on the syntheses and properties of active peptides containing aminooxy acids.[15–18]

Physical and chemical properties of 2-aminooxy acids and their derivatives have also been the subject of many studies.[19–22] It has been suggested that they do not form complexes with metal ions.[23] Our potentiometric investigations have shown, however, that these ligands interact with metal cations and stability constants of the complexes formed have been established.[24] Some complexes have been isolated in the solid state and preliminary results reported earlier.[25] The crystal and molecular structure of diaquobis(2-aminooxy-propanoate)copper(II) dihydrate has been reported.[26]

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In this paper we present experimental results of an investigation of the spectroscopic and magnetic properties of monohydrate and anhydrous complexes of the title metals and ligands.

EXPERIMENTAL

Preparation of the compounds

The 2-aminooxy acids and their methyl esters were synthesized by the methods described in the lterature.[23] The starting reagents were commercially available amino acids.

Aquobis(2-aminooxypropanoate) copper(II)

An aqueous solution of the sodium salt of 2-aminooxypropanoic acid was prepared from equivalent quantities of the aminooxy acid chloride and sodium bicarbonate.

The solution was warmed to 60°C and added to a warm solution of copper(II) chloride with stirring. The blue precipitate which settled out on cooling was filtered off, washed with small amount of water and recrystallized from water. A mole ratio (ligand to metal) of 2:1 was used. The remaining copper(II) complexes as well as the nickel(II) compounds were prepared by essentially the same procedure. The products, however, were recrystallized from ethanol or from an ethanol/water mixture in the case of 2-aminooxy-3-phenylpropanoic acid complexes.

Bis(methyl-2-aminooxypropanoate)cobalt(II) chloride

An ethanol solution of anhydrous cobalt(II) chloride was added with stirring to a hot ethanol solution of the methyl ester of 2-aminooxypropanoic acid. The resulting mixture (mole ratio of ligand to metal 2:1) was stirred at 60°C for 30 min. The deep blue precipitate which formed after cooling was filtered off and recrystallized from ethanol. The remaining cobalt(II) complexes were prepared in a similar way. All the complexes were stored in a desiccator over silica gel. The results of chemical analyses are collected in Table I.

Spectroscopic and magnetic measurements

Infrared spectra were recorded with a Perkin-Elmer 620 spectrophotometer in nujol mull and KBr disks. Electronic reflectance spectra were recorded on Unicam SP-700 and Hitachi 356 spectrophotometers equipped with the standard reflectance accessory.

Esr spectra were obtained at room temperature with a JES-ME-3X spectrometer, at a frequency of 9.191 GHz. Diphenylpicrylhydrazyl was used as a frequency calibrant.

Magnetic susceptibility was measured in the temperature range 300 K to 77 K by the Gouy method, using $HgCo(SCN)_4$ as the calibration standard. Corrections for the diamagnetism of the ligands were applied.

All the physical measurements were carried out using polycrystalline samples of the pure compounds.

TABLE I

Elemental analyses for the complexes.

Complex[a]	Calculated (%)			Found (%)		
	C	H	N	C	H	N
Cu(2-NH$_2$O-pro)$_2$·H$_2$O	24.87	4.87	9.66	24.96	4.55	9.52
Cu(2-NH$_2$O-pen)$_2$	36.24	6.15	8.54	36.86	6.30	8.35
Cu(2-NH$_2$O-4-mpen)$_2$	40.50	6.80	7.87	40.57	6.87	7.61
Cu(2-NH$_2$O-3-phpro)$_2$	51.00	4.66	6.60	51.30	4.90	6.81
Ni(2-NH$_2$O-eth)$_2$	20.12	3.38	11.72	19.80	3.48	11.45
Ni(2-NH$_2$O-pro)$_2$	27.01	4.51	10.49	26.80	4.70	10.39
Ni(2-NH$_2$O-4-mpen)$_2$	41.01	6.89	7.98	40.92	6.71	7.85
Ni(2-NH$_2$O-3-phpro)$_2$	51.59	4.81	6.68	51.40	4.92	6.59
Co(2-NH$_2$O-proMe)$_2$Cl$_2$	26.10	4.93	7.61	26.12	4.89	7.55
Co(2-NH$_2$O-butMe)$_2$Cl$_2$	30.32	5.60	7.07	30.25	5.50	7.21
Co(2-NH$_2$O-hexMe)$_2$Cl$_2$	37.18	6.69	6.19	37.02	6.58	6.05
Co(2-NH$_2$O-4-mpen)$_2$Cl$_2$	37.18	6.69	6.19	36.98	6.66	6.12

[a] Abbreviations used throughout: 2-NH$_2$O-pro = 2-aminooxypropanoate; 2-NH$_2$O-pen = 2-aminooxypentanoate; 2-NH$_2$O-4-mpen = 2-aminooxy-4-methyl pentanoate; 2-NH$_2$O-3-phpro = 2-aminooxy-3-phenylpropanoate; 2-NH$_2$O-eth = 2-aminooxyethanoate; 2-NH$_2$O-proMe, 2-NH$_2$O-butMe, 2-NH$_2$O-hexMe and 2-NH$_2$O-4-mpenMe = methyl ester of 2-aminooxypropanoic, 2-aminooxybutanoic, 2-aminooxyhexanoic and 2-aminooxy-4-methylpentanoic acids, respectively.

RESULTS AND DISCUSSION

Copper(II) complexes

Electronic spectra are similar to those observed for copper(II) complexes with amino acids.[27] The absorption maxima are within the range 15 000–16 000 cm^{-1} (Table II). The bands of analogous complexes with amino acids are shifted towards higher frequencies and fall within the range 15 200–16 800 cm^{-1}.[28–31] This can be well examplified by copper(II) complexes with 2-aminopropanoic and 2-aminooxypropanoic acids whose absorption maxima are at 16 800 and 15 200 cm^{-1}, respectively. This may be due to the markedly lower basicity of the aminooxy group of 2-aminooxy acids and the higher acidity of the carboxyl group as compared to analogous amino acids.[24] The position of the bands and shape of the spectra seem to suggest a centrosymmetric structure for the 2-aminooxy acid complexes.

The magnetic susceptibility measurements revealed no detectable exchange interactions. The magnetic moments take values from 1.86 to 1.91 B.M. and are close to those of distorted octahedral copper(II) complexes with amino acids. The esr spectra reveal three g values (Table II). This seems to indicate axial symmetry.

Nickel(II) complexes

Electronic reflectance spectra of nickel(II) complexes with 2-aminooxy acids reveal three sets of bands (Table II). A closer examination of the spectra yields some interesting information. It can be seen that the spectra of the first two complexes, *i.e.* with 2-aminooxyethanoic and 2-aminooxypropanoic acids, reveal three bands. These are characteristic for octahedral complexes for which three spin-allowed transitions are expected.[32] The position of the bands at about 8800, 16 800 and 26 300 cm^{-1} are close to those of anhydrous six-coordinate nickel(II) complexes with analogous amino acids.[33]

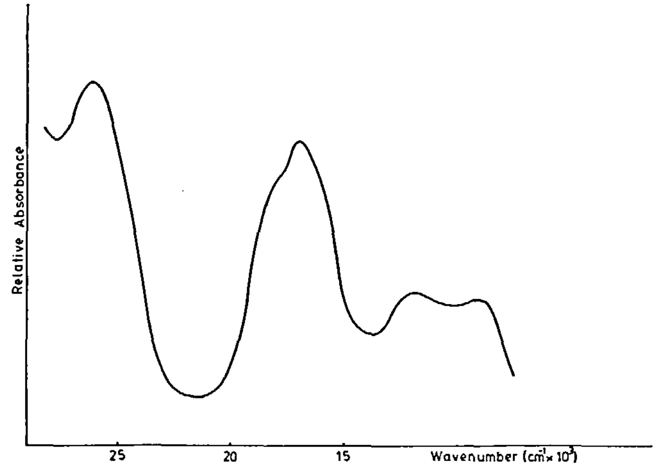

FIGURE 1 Electronic reflectance spectrum of $Ni(2\text{-}NH_2O\text{-}3\text{-}phpro)_2$.

TABLE II

Diffuse reflectance spectral data, magnetic moments and g values for Cu(II) and Ni(II) complexes of 2-aminooxy acids and Co(II) complexes with some of their esters.

Complex	Colour	μeff (B.M.)	g			Band maxima (cm^{-1})
			g_1	g_2	g_3	
$Cu(2\text{-}NH_2O\text{-}pro)_2 \cdot H_2O$	blue	1.91	2.09	2.17	2.22	15 000
$Cu(2\text{-}NH_2O\text{-}pen)_2$	blue	1.90	2.08	2.20	2.29	15 400
$Cu(2\text{-}NH_2O\text{-}4\text{-}mpen)_2$	blue	1.89	2.07	2.22	2.38	15 600
$Cu(2\text{-}NH_2O\text{-}3\text{-}phpro)_2$	blue-violet	1.86	2.07	2.13	2.23	16 000
$Ni(2\text{-}NH_2O\text{-}eth)_2$	light-blue	3.02				26 300, 16 800, 12 100, 8 900
$Ni(2\text{-}NH_2O\text{-}pro)_2$	light-blue	3.07				26 300, 16 800, 12 200, 8 800
$Ni(2\text{-}NH_2O\text{-}4\text{-}mpen)_2$	light-blue	3.14				28 400, 26 000, 16 700, 12 000, 8 900
$Ni(2\text{-}NH_2O\text{-}3\text{-}phppro)_2$	blue	3.15				28 700, 26 100, 17 900, 17 000, 12 000, 9 000
$Co(2\text{-}NH_2O\text{-}proMe)_2Cl_2$	blue	4.53				19 100, 16 500, 16 000, 15 100, 14 500, 6 300, 5 600, 5 300, 5 200
$Co(2\text{-}NH_2O\text{-}butMe)_2Cl_2$	blue	4.55				22 000, 18 800, 16 200, 15 900, 15 600, 14 900, 14 400, 6 300, 5 700
$Co(2\text{-}NH_2O\text{-}hexMe)_2Cl_2$	blue	4.65				21 300, 16 400, 16 000, 15 000, 14 500, 6 300, 5 600, 5 200
$Co(2\text{-}NH_2O\text{-}4\text{-}mpenMe)_2Cl_2$	blue	4.63				20 600, 19 400, 18 600, 16 000, 15 000, 14 400, 6 400, 5 700

The spectra of the complexes of 2-aminooxy-4-methylpentanoic and 2-aminooxy-3-phenylpropanoic acids are more complicated. This is illustrated in Figure 1. The bands predicted for spin-allowed transitions are split. Such splitting has also been observed in the spectra of nickel(II) complexes with other organic ligands[34] and the result suggests that deviation from octahedral geometry is greater than in the above cases. This is probably due to steric effect involving the bulky hydrocarbon side groups of the ligands.

Variable temperature magnetic measurements did not show any signs of magnetic exchange down to 81 K. All of the complexes are spin-free, having magnetic moments in the range 3.02–3.15 B.M. These values are close to those of analogous complexes with amino acid ligands[33] and indicate that the nickel(II) complexes with aminooxy acids have essentially octahedral stereochemistry.

The i.r. spectra of the coordinated 2-aminooxy acids can be used to indicate the mode of binding with the central ions. The spectra of the copper(II) and nickel(II) complexes are similar so in Table III only the data for the former are collected. There are four potential donor atoms in 2-aminooxy acid ligands, two oxygen atoms of carboxylate group as well as oxygen and nitrogen atoms of the aminooxy group. The i.r. spectra of the free ligands are broadly similar to those reported by Sohár *et al.*[20] In the copper(II) complexes the asymmetric stretching vibrations of the carboxylate group centred around 1606 cm^{-1} are very close to those observed for the free ligands. This is similar to copper(II) complexes of amino acids[35-39] in which the carboxylate group is bound to metal ion.

The bands representing the symmetric vibrations of the carboxylate group in the copper(II) complexes are observed in the approximate range 1400–1410 cm^{-1} and are slightly but distinctly shifted towards lower energies when compared to the free ligands. This effect was also found earlier for amino acid complexes.[35-39]

The simple conclusion is that the binding mode of the carboxylate group is very similar to that found for amino acids.

The more considerable changes upon metal ion coordination are seen in the bands of the aminooxy group. The infrared spectra of the free 2-aminooxy acids reveal four bands within the 2000–3050 cm^{-1} region; just above 3000 cm^{-1}, and around 2600, 2380 and 2090 cm^{-1}. The coordination of the amino group to a metal ion leads to drastic changes in this part of the spectrum and new bands are observed at about 3300, 3230 and 3100 cm^{-1}. All these bands can be assigned to stretching vibrations of the NH_2 group as in related complexes of amino acids.[35-39] The strong band in the 1645–1621 cm^{-1} range (asymmetric deformation of NH_3^+) vanishes and a single band of strong intensity appears at 1570–1558 cm^{-1}. The latter band can be assigned to deformation of the NH_2 group bound to the metal ion. Distinct variations of band positions upon metal ion binding are also observed for the ONH_2 group. Free aminooxy acids are characterized by a strong band in the 1290–1275 cm^{-1} range which corresponds to the stretching vibration of the aminooxy CO group. Metal ion coordination shifts this band 38–52 cm^{-1} to lower energies (Table III).

Less distinct variation upon metal ion coordination is observed for the NO stretching vibration which in free ligands is centred at 1012–990 cm^{-1} and in the copper(II) complexes in the 1040–1035 cm^{-1} range.

All these data lead to the conclusion that the anhydrous copper(II) and nickel(II) bis(2-aminooxy acid) complexes have a six-coordinate structure. Thus the ligands are both chelating and bridging for they coordinate to one metal ion *via* their nitrogen atom and one oxygen atom of the carboxylate group and to a neighbouring metal ion *via* the other oxygen atom of the COO^- group (Fig. 2). It should be pointed out that

TABLE III

Characteristic infrared frequencies (cm^{-1}) of 2-aminooxy acids and their copper(II) complexes.

2-NH_2O-pro		2-NH_2O-pen		2-NH_2O-4-mpen		2-NH_2O-3-phpro		Assignment
Ligand	Complex	Ligand	Complex	Ligand	Complex	Ligand	Complex	
	3310s		3307s		3305s		3305s	NH_2 stretch
	3210s		3240s		3238sb		3230mb	
	3090sb		3115s		3100m		3108m	
3050m		3040m		3030sb		3050sb		NH_3^+ stretch
2670sb		2700s		2660mb		2550m		
2340m		2480s		2350m		2380m		
2100m		2080m		2090w		2080w		
1645s		1628s		1634s		1621s		NH_3^+ def.
1608s	1610s	1608s	1606s	1600s	1608s	1596s	1602s	COO^- asym. stretch
	1568s		1560s		1570s		1558s	NH_2 scissors
1540		1523s		1535m		1545s		NH_3^+ sym. def.
1415m	1410m	1412s	1408m	1410m	1402m	1408m	1400s	COO^- sym. stretch
1290s	1238m	1281m	1238m	1278s	1238m	1275m	1237s	CO stretch in CON
990m	1040m	1008s	1035s	1005s	1033m	1012m	1035m	NO stretch in CON
835s	855m	858m	825m	845s	822m	848s	840s	COO^- scissors
682s	685m	670s	667m	684s	660m	686s	682s	COO^- wagging

the energy of the band maxima of the copper(II) complexes changes in the order 2-NH_2O-pen < 2-NH_2O-4-mpen < 2-NH_2O-3-phpro. This seems to indicate that tetragonal distortion from an octahedral structure follows the same sequence and may be explained in terms of increasing elongation of the axial bonds between central ions and the bridging oxygen atom.[27,31]

The monohydrate copper(II) complex also possesses a six-coordinate structure. Two of the 2-aminooxypropanoic acid residues are chelated to the central ion forming two six-membered rings. It is difficult, however, to elucidate unambiguously which of the donors complete the structure. In the analogous monohydrate copper(II) complexes with amino acids the water molecule can act as a unidentate[40] or a bridging[31] ligand.

In the former case dimeric structures arise in which the copper(II) ions are linked by bonds from the free carboxyl oxygen atom. If the water molecule acts as a bridging ligand a polymeric structure is formed. The data obtained here are unable to provide direct information on the role the water molecule plays in the Cu(2-NH_2O-pro)$_2$.H_2O complex.

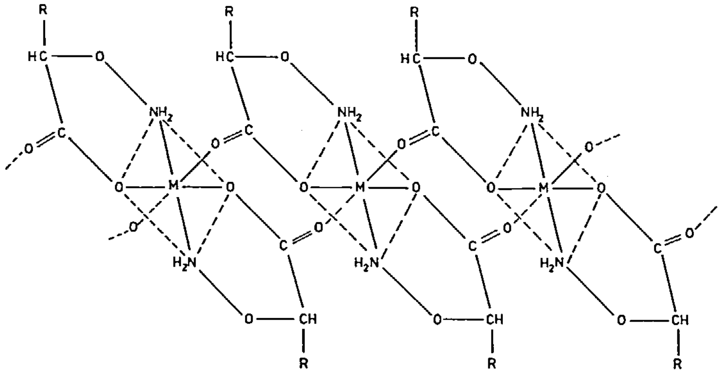

FIGURE 2 Proposed structure of the anhydrous copper(II) and nickel(II) complexes with 2-aminooxy acids.

Cobalt(II) complexes

By analogy with the above cases, one can predict that cobalt(II) would also be six-coordinate with 2-aminooxy acids. This conclusion is supported by the fact that cobalt(II) complexes with amino acids have the same structure.[41] For this reason we have limited our investigations to cobalt(II) complexes with some of the aminooxy acid esters.

The absorption maxima of the complexes are collected in Table II and exemplified in Fig. 3. The shape of the spectra and position of the bands suggests that the central ion lies in a tetrahedral environment. In each of the spectra two sets of bands can be distinguished, one in the visible and the other in the near infrared region. The former multiple absorption appears between 16 000–14 400 cm^{-1} and may be attributed to the $^4A_2 \rightarrow {}^4T_1(P)$ transition. Splitting of the band is probably due to interaction with the doublet state through spin-orbit coupling.[42]

TABLE IV

Characteristic infrared frequencies (cm^{-1}) of 2-aminooxy acid esters and their cobalt(II) complexes.

2-NH_2O-proMe		2-NH_2O-butMe		2-NH_2O-hexMe		2-NH_2O-4-mpenMe		Assignments
Ligand	Complex	Ligand	Complex	Ligand	Complex	Ligand	Complex	
3350s	3390s	3345sb	3380sb	3350m	3380s	3355m	3385sb	NH_2 stretch
3280m	3300s	3270m	3190sb	3260m	3290m	3280m	3300m	
3170m	3190s	3170m	3185m	3160m	3195sb	3170m	3185sb	
1752s	1745s	1748s	1746sb	1750s	1743s	1748s	1748s	CO stretch
1590s	1595s	1588m	1610m	1586	1590m	1590m	1600s	NH_2 asym. def.
1150s	1180m	1144s	1170s	1140m	1165s	1140s	1160m	CO stretch in CON
1080s	1055m	1062s	1040m	1075s	1053s	1070m	1056m	NO stretch in CON

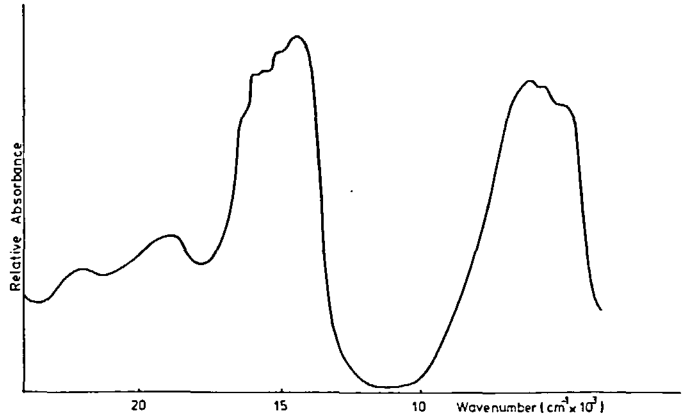

FIGURE 3 Electronic reflectance spectrum of $Co(2\text{-}NH_2O\text{-}butMe)_2Cl_2$.

The second set contains three strong bands in the 6400–5200 cm^{-1} region. Its complexity is caused by the components of the $^4T_1(F)$ level, which become allowed transitions in C_{2v} symmetry. The particular components of the ν_2 band can be attributed, in order of increasing energy, to the transitions $^4A_2 \rightarrow {}^4B_1$, $^4A_2 \rightarrow {}^4A_2$ and $^4A_2 \rightarrow {}^4B_2$.[43] The proposed structure is supported by the magnetic moments, which are in the range 4.53–4.63 B.M. and are characteristic for tetrahedral cobalt(II) complexes.[43]

I.r. spectral data for the cobalt(II) complexes are collected in Table IV. These data show that the binding of cobalt(II) ions to the 2-aminooxy acid esters causes major variations in the bands corresponding to the aminooxy group of the ligands. The stretching frequencies of the NH_2 group shift towards higher energies by 15–40 cm^{-1}. An analogous tendency is also observed in the case of deformation vibrations of the group.

The stretching frequencies of the aminooxy CO group shift from 1150–1140 cm^{-1} to 1180–1160 cm^{-1} when cobalt(II) ion binds to the ligand. Also, the NO stretching bands move about 24 cm^{-1} towards lower energy in the complex. The vibrations of the ester group do not indicate any distinct change upon coordination and it seems that this group does not participate in bonding.

The available data indicate that in the complexes of cobalt(II) with 2-aminooxy acid esters, two molecules of ester, bound *via* nitrogen atoms, and two chloride ions form a distorted tetrahedral structure around the central ion.

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