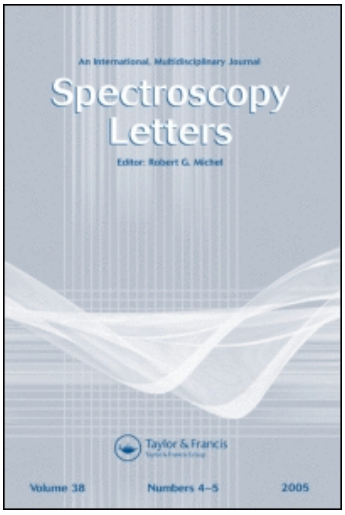

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The Spectral Study on the Ni(II) Semisepulchrates

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THE SPECTRAL STUDY ON THE Ni(II) SEMISEPULCHRATES

Key Words: Ni(II) semisepulchrates, IR-Raman, UV-VIS, NMR, gausssian deconvolution, isotope shifts, crytal field parameters

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ABSTRACT

The semisepulchrate type complexes Ni^{2+}bisperchlorate tris(((aminoethyl)amino)methyl)amine and Ni^{2+}perchloratechloride tris(((aminoisopropyl)amino)methyl)amine have been obtained and characterized by means of IR, Raman, UV-VIS and proton NMR study. Vibrational spectra have been interpreted on the basis of the deuteration

and metal isotope shift data. The capping group vibrations were found near 890 cm^{-1}, 630 cm^{-1} and 470 cm^{-1}. Crystal field parameters were estimated from the UV-VIS spectra. The Dq parameter equals 1232 cm^{-1} for the first complex and 1224 cm^{-1} for the second, Racah'a parameter B equals 767 cm^{-1} and 787 cm^{-1} respectively. The position of $N(CH_2)_3$ capping group proton resonances were found to be in the region 161-159 ppm.

INTRODUCTION

The cryptate effect is of a big importance in coordination chemistry because it allows for design of ligands which display enhanced complex stability and metal ion selectivity. Condensation of $NiCl_2$ with formaldehyde, ethylenediamine and ammonia gives rise to two types of Ni^{2+} complexes: sepulchrates and semisepulchrate [1-3] which are formally cryptands.

The syntheses and the stuctural data of Ni^{2+} bisperchlorate tris(((aminoethyl)amino)methyl)amine (denoted I thereafter) and Ni^{2+}perchloratechloride tris(((aminoisopropyl)amino)methyl) amine (denoted II thereafter) have been recently presented [4,5]. In the present work the spectral studies on I and II have been carried out. The UV/VIS absorption, NMR and the vibrational spectra for natural abundance and deuterated analogs are presented.

EXPERIMENTAL

The infrared spectra were measured on a Specord 80 spectrophotometer (in KBr pellets, 4000-200cm^{-1}) and on a Perkin Elmer 180 spectrophotometer as nujol mulls (500-50 cm^{-1}).

The Raman spectra were recorded using Jobin-Yvon U100 spectrophotometer equipped with an Ar^+ cw laser using 457.9 nm exciting line, by rotating disc technique.

UV/VIS absorption spectra of 0.1M aqueous solution of complex I, II and $[Ni(en)_3]^{2+}$ were recorded in the range of 13000-36000 cm^{-1} with a Hitachi 356 UV/VIS spectrophotometer interfaced to IBM PC/XT computer.

^1H NMR ivestigations employed a GE NMR QE-300 instrument, D_2O solvent and DSS standard.

Preparation

The complexes I and II were synthesised by procedures described in [4] and [5].

The deuterated analogs were obtained from I and II by a twofold recrystallisation from D_2O.

The ^{62}Ni labelled (I) complex was prepared using $^{62}NiCl_2$.

$[Ni(en)_3]Cl_2$ complex was obtained according to the method described in [6].

RESULTS AND DISCUSSION

The X-ray structures [4,5] reveal that the title compounds contain the discrete ions $(C_9H_{33}N_7Ni)^{2+}$ (I) and $(C_{12}H_{33}N_7Ni)^{2+}$ (II), as well as perchlorate and chloride ions. The symmetry point group of both cations is C_3, with threefold axes passing through the Ni and capping nitrogen atom (Figure 1).

Based on the C_3 point group, the normal modes can be classified as Γ_{vib}=42A+84E for I and Γ_{vib}=51A+102E for II, all the modes being infrared and Raman active. The number of bands observed in the vibrational spectra is much lower than that expected (Table 1). It is probably caused by the overlap of some bands due to

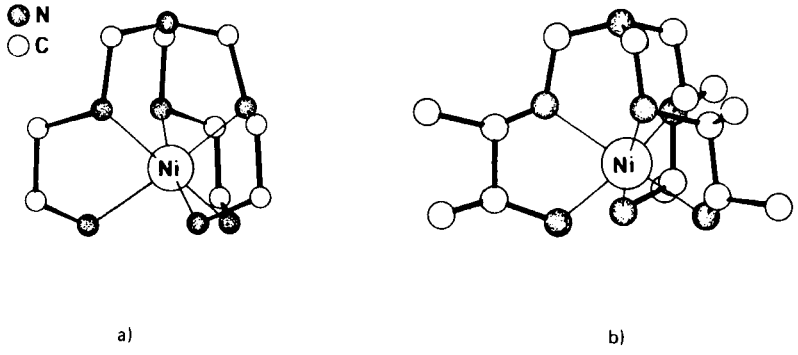

Fig. 1. Structure of the complexes
a) Ni^{2+}bisperchlorate tris(((aminoethyl)amino)-methyl)amine,
b) Ni^{2+}perchloratechloride tris(((aminoisopropyl)-amino)methyl)amine.

very similar energy of vibrations. On the other hand, a very good agreement between the positions of IR and R bands is observed.

The vibrations of the perchlorate ions are found to be typical of the free ClO_4^- ion (A_1,E,$2F_2$) [7].

The assignment of the stretching and deformation modes of the ligand has been made on the basis of the frequency shift observed as a result of deuteration and the literature data [8]. We have compared our assignments with those proposed by D.B.Powell et al [9] and A.M.A.Bennett et al [10] for ethylenediamine and $M(en)_3^{2+}$ complexes.

The vibrations of $N(CH_2)_3$ groups of the semisepulchrate ions were of our special interest. No previous information on that subject are available in the literature.

TABLE 1

Vibrational spectra of Ni^{2+}bisperchloratetris(((aminoethyl)amino)methyl)-amine and Ni^{2+}perchlorate-chloride tris((aminoisopropyl)amino)methyl)-amine [cm^{-1}].

I			II			
IR		R	IR		R	Assignment
$^{NA}Ni(\Delta_1)$	N(D)	^{NA}Ni	$^{NA}Ni(\Delta_2)$	N(D)	^{NA}Ni	
1	2	3	4	5	6	7
3340vs	2496s	3340m	3332vs	2484vs	3330m	$\nu_{as}NH_2$
3296vs	2444s	3300vs	3240vs	2404s	3245s	$\nu_{s}NH_2$
3182m	2428s	3185v	2348vs	2348vs	3166m	νNH
2948m	2948m	2950vs	2972s	2972s	2969s	$\nu_{as}CH_2, \nu_{as}CH_3$
2890m	2892m	2895vs	2932s	2930s	2930vs	$\nu_{s}CH_2, \nu_{s}CH_3$
			2880s	2880s	2877s	$\nu_{s}CH$
					2778vv	overtones
	2372m				2733vv	
	2348m				2660vv	

(cont.)

TABLE 1. (cont.)

1	2	3	4	5	6	7
1612m	1230s	1614v,br	1612m	1229vs	1610vs	$\delta sciNH_2$
1592m	1145s					
			1475m,sh		1471m	$\delta asCH_3$
1470m	1470m	1471m	1460m	1462s	1460s	$\delta sciCH_2$
			1450m	1450m,sh	1450m,sh	
1440m	(1100)ov	1436m	1440m	1120s	1438m	δNH
1372m	1372m	1375m	1405m	1410m		δvCH_2
1350v	1352v	1353v	1392m			
			1382s	1382s	1387m	$\delta symCH_3$
			1368m	1375m,sh	1375m	
			1337v	1352m	1366m	δCH
1278m	1270m	1278m	1298v	1282v	1297m	$\delta tCH_2+\delta vNH_2$
1254m	(1000)ov	1254vv	1252s	992s	1250vv	δtNH_2
1205m	1205m	1207v	1219v		1218vv	δtCH_2
			1200s	1200s	1200v	δrCH_3
1140m,sh		1130m	1140vs	1136vs	1140v	
1115vs	1115vs	1120m				$\nu CN+\nu CC$

1105vs	1110vs	1100m,br				
1092vs	1092vs	1085m	1090vs	1104vs	1082m	$\nu ClO_4^-(F_2)$
			1070vs	1074vs		
1058vs,sh	1050vs	1059m	1055vs,sh			
1045vs,sh	1034vs	1041m	1035s		1040w	$\nu CC+\nu CN+\nu NC_3(E)$
			1018vs	1016vs	1016w	
990vs,sh	999vs	988m	984m	940vw	980	
980vs	800m	970w	965s	855m	963w	
960s	860m		930w	840m		$\delta rNH_2+\nu CN$
948m	752m	948m,sh				
		934vs			930vs	$\nu ClO_4(A_1)$
930m,sh	912m	913s	920w		913s	$\nu CN+\delta rNH_2$
875m	885s	888s	890m	890m	888m	$\nu NC_3(A)$
			879w	880w,sh	874m	ωCH
832s	724m	839w	843w	818m	843m	δrNH_2
			809w		809m	
670vw	670vw	680vw				δrCH_2

(cont.)

TABLE 1. (cont.)

1	2	3	4	5	6	7
659m	670v	670v	δCCC			
630vv,sh	635m,sh		635m	630v,sh		$\delta NC_3(E)$
624vs	626vs	624s	624vs	624vs	623vs	$\nu ClO_4(F_2)$
550vv,sh	550v					skeletal vib.
535v						
494s	492m	495v	476v	470v	450m,sh	$\delta NC_3(A)$
		462s			457s	$\nu ClO_4(E)$
458v	458v		433v		433v	skeletal vib.
434m(-4)	428v	418s(-4)	416m	412v	413v	νNiN
380v		380v	400v	394s	389m	skeletal vib.
361s	354s	363v	378vv			
338vv		340vv	360v,sh			
			355v		351m	
316v	312v	316m	344v	338m	341	
282v	278v	283m(-3)	284v,sh	276v,sh	284v	νNiN
268m(-2)	266v	270m	270v,sh		270v	skel.vib.+νNiN

		220s	264m	264m	252v	skeletal vib.
				246v		
224m(-4)	224m	205v(-10)	234v	246v	218v	δNNiN
207v	200v				204v	
168vv	154v	164v	190v	182v	169v	lattice vib.
	118s	155v	150v	154v	154v	
		107m	110s	110s	107s	
92s	84s				90m	

Abbreviation:

$\Delta_{1,2}=\nu(^{NA}Ni(C_9H_{27}N_7)^{2+})-\nu(^{62}Ni(C_9H_{27}N_7)^{2+})$

N(D)-deuterated species.

Howe and Taylor [11] have examined the vibrational spectra of trimethyloxonium and trimethylammonium cations (C_{3V} symmetry) and carried out the normal coordinate analyses for them. They have located NC_3 group stretchings at 980 cm^{-1}(E) and 800 cm^{-1} (A_1), the deformations at 480 cm^{-1} (A_1) and 400 cm^{-1} (E).

We have found the skeletal stretching modes of NC_3 group in a little higher frequency region (see Table 1). The E vibrations have been not uniquevocally identified, Because they occure in the region of many very intense skeletal vibrations of the amine part of the ligand and $\nu(ClO_4)$ (F_2) vibration. The strong and medium intensity bands which appear near 890 cm^{-1} in the IR and R spectra of I and II, shifted to higher wavenumbers by 2-10 cm^{-1} after deuteration and were assigned to stretching vibrations (A modes) of capping groups. The deformation modes give rise to bands observed in the IR spectra at 630 cm^{-1} (E) and in Raman spectra at 470-490 cm^{-1} (A).

The stretchings of metal-nitrogen bonds appear in the region 450-270 cm^{-1} in the complexes studied. Strong bands located at 434 cm^{-1} in the IR and at 418 cm^{-1} in the Raman spectra of I are sensitive to ^{62}Ni labelling and shift to lower wavenumbers by 4 cm^{-1}. The deuteration of the complex also causes the lowering of the position of these bands, so reasonably they are assigned to ν(Ni-N) (E) stretching modes.

In the spectra of II, the ν(Ni-N)(E) was located at 416 cm^{-1} (IR) and 413 cm^{-1} (R).

The A mode stretchings of coordination bonds were found at 282 cm^{-1} (IR) and 283 cm^{-1} (R) ($\Delta\nu$ after ^{62}Ni labelling equals 3 cm^{-1}) for I, and at 284 cm^{-1} (IR,R) for II. These bands are also sensitive to deuteration.

Bennett and coworkers [10] have studied the IR spectra of $[Ni(en)_3]^{2+}$ and assigned the 410 cm^{-1} and 334 cm^{-1} bands to the Ni-N stretching modes (E and A_1,

respectively), however they have not performed any isotopic labelling on that complex.

The N-Ni-N deformation modes, in view of the deuteration and ^{62}Ni substitution sensitivity (tab.1) for I and II are found in the region 240-200 cm^{-1}, similarly to Bennett's assignment for $[Ni(en)_3]^{2+}$ complex [10].

All the measured UV/VIS absorption spectra were analysed by an earlier described computer method [12]. The $[Ni(en)_3]^{2+}$ spectrum was also analysed for comparison. The spectra were resolved into component bands. Transition energies determined on the grounds of resolution gave the basis for calculating the crystal field parameters. In the course of analysis the results of spectrum decomposition were verified by comparison with the predictions of the crystal field theory. It allowed to identify and assign all bands occuring within the investigated range to their corresponding transitions. It was also possible to determine precisely crystal field parameters. The process of resolution of the experimental contour into component bands was performed by using the modification of Non-Linear Least Squares algorithm [13]. Crystal field parameters were calculated based on the energy matrices from work [14]. The SIMPLEX method was used. All calculation were carried out on an IBM PC/XT compatible computer.

All the measured spectra (complex I, II and $[Ni(en)_3]^{2+}$) show two crystal field bands corresponding to spin-allowed transitions $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (O_h symmetry) and the shoulders of two bands from the outside of the measure range (Figure 2) - the first one (near red) corresponding to spin-allowed transition $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ and the second one (UV) to molecular

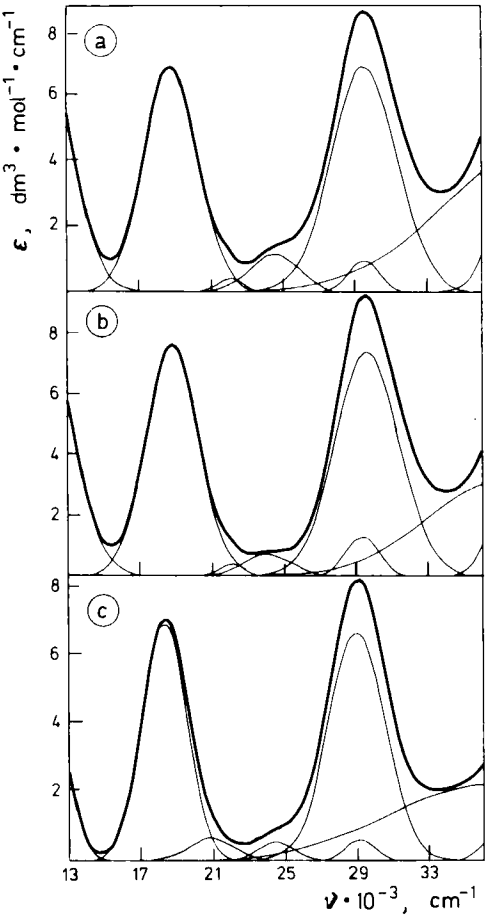

Fig. 2. Resolved electronic absorption spectra of complexes:

a) [Ni tris(((aminoethyl)amino)methyl)amine]$^{2+}$,

b) [Ni tris(((aminoisopropyl)amino)methyl)amine]$^{2+}$,

c) [Ni(en)$_3$]$^{2+}$.

transition. The bands corresponding to spin-forbidden transitions are strongly overlapped.

Crystal field bands appearing in the measured range do not show splitting. For this reason we assumed O_h symmetry as a good model for description of all the analysed complexes. A slight trigonal distortion from O_h symmetry of the coordination sphere (NiN_6 chromophore) can be omitted as nonsignificant in this analysis. The doublet, which one can observe in near red for I and II (out of our measure range - about 11900 and 12600 cm^{-1}) is rather connected with intensity exchange between spin-allowed transition $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ and spin-forbidden transition $^3A_{2g}(F) \rightarrow {}^1E_g^1$, then with decreasing the complex symmetry. As was pointed out by Jörgensen [15], this area of the spectrum corresponds to the energy crossover point of the $^3T_{2g}$ and ^1E_g energy levels. These terms can not actually coincide and have a minimum separation. At the same time, the spin-forbidden transition corresponding to the ^1E_g level will "borrow" intensity from the spin-allowed transition corresponding to the $^3T_{2g}$ level. The two energy levels are actually mixed and neither of the two peaks can be said to correspond to a pure transition to either of the two energy levels. For this reason it seems reasonable to determine the crystal field Dq parameter from the second $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and third $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ d-d spin-allowed transitions.

All the measured spectra were resolved into component bands (Fig. 2). Transition energies determined from the resolution were used for the calculation of crystal field parameters. Spin-allowed and spin-forbidden transition energies assigned to the respective terms, as well as crystal field parameters for all the analysed complexes are given in Table 2.

TABLE 2

Crystal field transition energies and crystal field parameters of complexes I, II and $[Ni(en)_3]^{2+}$.

Transition	Energy $[cm^{-1}]$					
	I		II		$[Ni(en)_3]^{2+}$	
	theor	exp	theor	exp	theor	exp
$^3A_{2g}(F) \rightarrow$						
$^3T_{2g}(F)$	12319		12241		11798	
$^3T_{1g}(F)$	18892	18892	18882	18882	18359	18359
$^3T_{1g}(P)$	29572	29572	29640	29640	28975	28975
$^1E_g^1$	13113		12924		12829	
$^1A_{1g}^1$	22138	22033	21955	22021	21780	20890
$^1T_{2g}^1$	25188	24582	24908	24078	24358	24484
$^1T_{1g}$	28776	29524	28601	29347	28119	29144
$^1E_g^2$	39069		38773		37837	
$^1T_{2g}^2$	39313		39029		38107	
$^1A_{1g}^2$	61214		60417		59341	
Dq $[cm^{-1}]$	1232		1224		1180	
B $[cm^{-1}]$	767		787		796	
C $[cm^{-1}]$	3626		3461		3385	
C/B	4.73		4.40		4.25	

TABLE 3

The ^{1}HNMR shifts observed for I and II complexes [ppm].

I	II	
15	15	CH axial
23	21	
93	-	impurities
83	85	CH equatorial
101	95	
159	160	$N(CH_2)_3$

Since complexes I,II and $[Ni(en)_3]^{2+}$ are very similar, their electronic absorption spectra differ very slightly in shape from each other. This similarity causes that the corresponding transition energies obtained from resolution process are almost the same, expecially for complexes I and II. The crystal field parameter Dq, which is a measure of the crystal field strenght, is higher for complexes I and II than that for $[Ni(en)_3]^{2+}$ but also very similar. The similarity of these three complexes is futther confirmed by the Ni-N bond lengths, which are equal 2.121Å [4], 2.127Å [5] and 2.120Å [16] respectively. Racah'a parameter B, which is closely related to the ionicity of the bond, is highest for $[Ni(en)_3]^{2+}$ and lowest for complex I. Changes in B parameter have the reverse order as compared to those of Dq parameter. All the discussed transition energies and crystal field parameters are in good agreement with those of similar Ni^{2+} complexes [17].

According to the assignments reported for several nickel diamine complexes [18,19], the most downfield resonances observed in the ^{1}H NMR spectra of I and II (Table 3) are attributed to the axial CH protons, the peaks observed in the region 80-120 ppm to the equatorial CH protons.

The broad peaks observed at 159 ppm for I and at 160 ppm for II are most probably the resonances of capping group methylene protons.

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