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Far-infrared Spectra of Mercaptoalkylamine Complexes with Ni^{II} and Pd^{II}*

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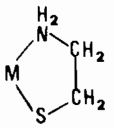
The far-infrared spectra of metal complexes of mercaptoethylamine and related ligands with Ni^{II} and Pd^{II} have been measured. Band assignments have been made based on isotope substitution of the metal (^{58}Ni–^{62}Ni or ^{104}Pd–^{110}Pd) and the amino group (NH_2–ND_2) of the ligand. The configuration of theMN_2S_2 skeleton has been determined by the observed number of the M–N and M–S stretching bands. The electronic spectra of the Ni^{II} complexes support the structures proposed by the far-infrared study.

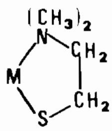
Introduction

There are various types of ligands with sulfur as donor atoms. They range from sulfides and thiolates which form relatively ionic bonds to dithienes[1] which form strong covalent bonds with metals. The chemistry of sulfur containing ligands has been reviewed by Livingstone[2], and the electronic spectra of metal complexes with sulfur ligands have been reviewed by Jørgensen.[3] Thus far, infrared studies have been made on metal complexes of the dithiocarbamato[4], xanthato,[5] and dithiooxalato ions[6], thioethers[7], cysteine[8] and methionine[9]. Recently, the infrared spectra of mono-[10] and di-thioacetylacetonato,[11] and dithiene[12] complexes with various metals have also been studied. No systematic studies have yet been made, however, on the far-infrared spectra of thiolato complexes with the first row transition metals. This may be due to two reasons: (1) The coordinated sulfur atom of thiolates is still nucleophilic enough to react with the second metal atom to form a polymeric species and (2) free thiolates are easily oxidized to form disulfides.

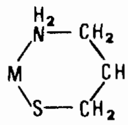
In this work, we have studied the vibrational spectra of Ni^{II} and Pd^{II} complexes of 2-mercaptoethylamine (MEA), its N,N-dimethyl derivative (MMEA) and 3-mercaptopropylamine (MPA) mainly because they can be obtained as monomeric square-planar complexes and a considerable amount of investigations has already been carried out on them.[13] The main purpose of this work was to determine the structure of the MN_2S_2 skeleton of these complexes (*cis, trans*) from far-infrared spectra. The MEA and MPA complexes are not soluble in any solvents and cannot be obtained in a crystalline form. Therefore, the dipole moments, NMR and UV spectra of these compounds cannot be measured in solution. However, the Ni^{II} complex of MMEA is soluble in chloroform and can be obtained in a crystalline form. An x-ray analysis on this compound[14] shows that the NiN_2S_2 skeleton is *trans*-planar. For $Ni(MEA)_2$, Jicha and Busch[15] proposed the *cis*-planar structure based on chemical evidence. However, their results do not exclude the possibility of fast isomerization from the *trans* to *cis* configuration when it is dissolved in DMF during the reaction with nucleophilic agents such as metal ions or alkyl iodide.



MEA Complex



MMEA Complex



MPA Complex

Experimental Section

Preparation of Compounds. $Ni(MEA)_2$,[13] $Pd(MEA)_2$[13] and $Ni(MMEA)_2$[15] were prepared according to the methods described in literature. $Pd(MMEA)_2$ was prepared for the first time in this work. It was prepared by a method similar to that used for $Ni(MMEA)_2$[15]: K_2PdCl_4 (479 mg, 1.5 mmol) was reacted with a slight excess of MMEA · HCl (475 mg 3.2 mmol) in aqueous ammonia for 15 minutes. The yellow solution was extracted twice with 20 ml chloroform.

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Evaporation of the chloroform solution left a yellow oil from which the Pd complex was obtained. It was recrystallized from a mixture of trichloroethylene and n-hexane. *Analysis*: Calcd for $C_8H_{20}N_2S_2Pd$: C, 30.52; H, 6.40; N, 8.60; S, 20.3%. Found C, 30.29; H, 6.43; N, 8.42; S, 20.25%.

$Ni(MPA)_2$ was prepared by adding 5 ml 2N NaOH solution to 20 ml aqueous solution of $NiCl_2 \cdot 6H_2O$ (188 mg, 0.8 mmol) and MPA · HCl (255 mg, 2 mmol). The complex was filtered off and washed several times with water, then with ethanol. *Analysis*: Calcd for $C_6H_{16}N_2S_2Ni$: C, 30.15; H, 6.73; N, 11.72; S, 26.82%. Found: C, 29.79; H, 6.73; N, 11.54; S, 26.62%.

The MEA–d_2 complexes were prepared by the same methods given above except that D_2O was used as the solvent instead of H_2O. All attempts to prepare $Pd(MPA)_2$ and $Pd(MBA)_2$ (MBA: 4-mercaptobutylamine) were unsuccessful.

MEA · HCl was purchased from Aldrich Chemical Co., Milkwaukee, Wisconsin. MPA · HCl and MBA · HCl were kindly furnished by Dr. H. M. Swartz, Marquette Medical School, Milwaukee, Wisconsin. All metal complexes containing metal isotopes were prepared on a milligram scale using metal isotopes purchased from Oak Ridge National Laboratory. The purity of metal isotopes was: ^{58}Ni (99.98%), ^{62}Ni (99.02%), ^{104}Pd (89.75%), and ^{110}Pd (96.98%).

Spectral Measurements

Infrared spectra were measured on a Beckman IR-12 (4000-250 cm^{-1}) and a Hitachi-Perkin-Elmer FIS-3 (410-33 cm^{-1}) infrared spectrophotometer. The KBr pellet technique was used for the 4000-300 cm^{-1} ragion, and the Nujol mull technique with polyethylene plates was used for the 410-33 cm^{-1} region. To observe small shifts due to metal isotopic substitution, the spectra were run on an expanded scale with a scanning speed of 2-4 cm^{-1}/min. Reproducibility of the spectra was checked by multiple scans over the desired frequency range Calibration of the frequency reading was made by recording the spectra of polystyrene, indene and water vapor.

The electronic spectra of the solid samples in Nujol mull were recorded on a Cary Model 14 recording double beam spectrophotometer. The spectrum of $Ni(MMEA)_2$ was also recorded in $CHCl_3$ solution.

Results and discussion

MMEA Complexes. According to X-ray analysis,[14] the NiN_2S_2 skeleton of $Ni(MMEA)_2$ is *trans*-planar and the whole molecule retains the C_i symmetry although the chelate rings are not planar. In this case, the *trans* structure seems to be preferred to the *cis* structure mainly because of the steric repulsion between the methyl groups of two MMEA ligands. For the *trans*-planar structure, one Ni–S and one Ni–N stretching mode should be infrared active. Furthermore, both of these modes are expected to give large shifts relative to others when ^{58}Ni of $Ni(MMEA)_2$ is substituted by ^{62}Ni.

Figure 1 ilustrates the far-infrared spectra of $^{58}Ni(MMEA)_2$ and its ^{62}Ni analog, and Table I lists the observed frequencies and isotopic shifts. These results show that two bands at 397.3 and 371.2 cm^{-1} of $^{58}Ni(MMEA)_2$ give large shifts (more than 3 cm^{-1}) relative to other bands by the ^{58}Ni–^{62}Ni substitution. Therefore, these two bands must be assigned to the Ni–S or Ni–N stretching mode. Although there is a possibility of vibrational coupling between these two modes, the 397.3 and 371.2 cm^{-1} bands have been assigned to the modes predominantly due to the Ni–S and Ni–N stretching vibrations, respectively, because of the following reasons: (1) In general, the metal-nitrogen stretching band is weaker than the metal-sulfur stretching band. This was confirmed for the MEA complexes; weaker bands in the 450-300 cm^{-1} region (M–N stretching bands) are always markedly shifted by the deuteration of the NH_2 group. (2) According to rule 1, the 394 cm^{-1} band of $Pd(MMEA)_2$ must be assigned to the Pd–N stretching mode since it is weaker than the 367 cm^{-1} band (Fig. 1). Then, the Pd–N stretching frequency of $Pd(MMEA)_2$ (394 cm^{-1}) becomes higher than the Ni–N stretching frequency of $Ni(MMEA)_2$ (371 cm^{-1}). This trend is in good agreement with that found in the trend of the M–N stretching frequencies of *trans*-bis(glycinato)palladium(II) and its Ni^{II} analog.[16]

Table I. Observed Frequencies and Band Assignments of $Ni(MMEA)_2$ and $Pd(MMEA)_2$ (cm^{-1})

$^{58}Ni(NMEA)_2$	$\Delta\nu^a$	$Pd(MMEA)_2$	Assignment
513.7	1.0	478	ring def. (A)
397.3	3.2	367	ν(M–S)
371.2	3.7	394	ν(M–N)
282.0	1.3	294	δ(NMS) (B) [b]
179.6	1.7	140	δ(NMS) (C) [c]
105.0	0	105	ligand

[a] $\nu(^{58}Ni)$–$\nu(^{62}Ni)$. [b] Bending mode involving the NMS angle inside the chelate ring. [c] Bending mode involving the NMS angle between two chelate rings.

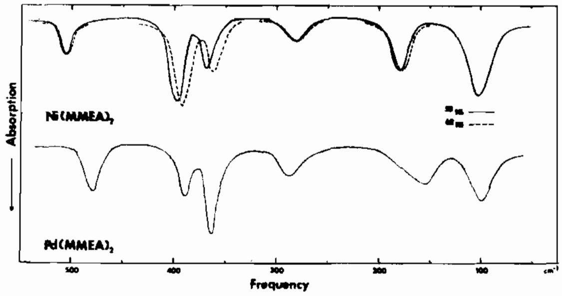

Figure 1. Far-infrared spectra of $Ni(MMEA)_2$ and $Pd(MMEA)_2$

$^{58}Ni(MMEA)_2$ exhibits three isotope sensitive bands in addition to the Ni–S and Ni–N stretching modes discusses above. As will be discussed later, these bands are assigned to the bending modes, A (513.7 cm^{-1}), B (282.0 cm^{-1}) and C (179.6 cm^{-1}). Figure 1 and Table I show that the spectrum of $Pd(MMEA)_2$ is very similar to that of $Ni(MMEA)_2$. It is, there-

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Table II. Observed Frequencies, Istopic Shifts and Band Assignments of Ni(MEA)$_2$, Pd(MEA)$_2$ and Ni(MPA)$_2$ (cm^{-1}).

Ni(MEA)$_2$			Pd(MEA)$_2$			Ni(MPA)$_2$			
ν(^{58}Ni)	Δν [a]	Δν [b]	ν(^{104}Pd)	Δν [c]	Δν [b]	Δν(^{58}Ni)	Δν [a]	Δν [b]	
550.4	2.9	35.8	535	3.0	53	515	3.0	25	Ring def (A)
479.1	1.7	18.1	500	2.0	33	490	2.0	12	
377.1 [d]	5.9 [d]	?	421	3.0	19.5	385.5	2.5	12.5	ν(M—N)
377.1 [d]	5.9 [d]	0.1	367.5	1.6	5.6	312.0	2.0	2.0	ν(M—S)
330.1	1.9	0.3	337.5	2.5	5.5	277.5	2.5	3.5	ν(M—S)
336.1	2.1	8.6	308.5	2.7	8.5	354.7	3.7	8.7	ν(M—N)
291.9	1.9	26.9	290.7	1.7	13.2	229.2	2.0	19.2	δ(NMS) (B)
167.2	1.1	2.7	155.5	2.0	0.4	165.0	2.0	0	δ(SMS) (C)
154.2	0.8	4.2	139	1.5	1.0	153.0	1.0	3.0	δ(NMN)
114.5	0.4	10.	123	0	0	128.0	1.0	3.0	ligand

[a] Δν=ν(^{58}Ni)—ν(^{62}Ni). [b] Δν=ν(MEA or MPA complex)—ν(NH$_2$-deuterated MEA or MPA complex). [c] Δν=ν(^{104}Pd)—ν(^{110}Pd). [d] Overlap of two bands. Frequencies (acervage values) were given down to the order of 10^{-1} cm^{-1} only when measure ments were made more than five times.

fore, safe to conclude that the structure of the Pd complex is also *trans*-planar.

Complexes of MEA and MPA. No X-ray analyses have been carried out on metal complexes of MEA and MPA since they have not yet been obtained in the crystalline form. Figure 2 shows the infrared spectra of Ni(MEA)$_2$, Ni(MPA)$_2$ and Pd(MEA)$_2$ below 550 cm^{-1}. The fact that these spectra are much more complicated than those of Ni(MMEA)$_2$ and Pd(MMEA)$_2$ (Figure 1) seems to suggest that the MN$_2$S$_2$ sekletons of these metal complexes are *cis*. If so, its local symmetry is C$_{2v}$, and two M—N and two M—S stretching modes should be infrared active. This conclusion does not change even if we consider the symmetry of the whole molecule since the highest possible symmetry for the *cis* complex is C$_{2v}$.

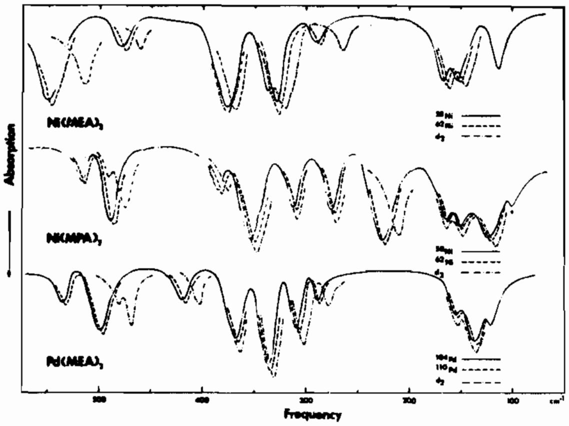

Figure 2. Far-infrared spectra of Ni(MEA)$_2$, Ni(MPA)$_2$ and Pd(MEA)$_2$.

As is seen in Figure 1 and Table I, the MMEA complexes exhibit three isotope-sensitive bands (one M—S stretching, one M—N stretching and one ring deformation) in the 450-200 cm^{-1} region. On the other hand, Ni(MEA)$_2$ exhibits four and Pd(MEA)$_2$ and Ni(MPA)$_2$ exhibit five metal-isotope sensitive bands in the same region (Figure 2 and Table II). ^{104}Pd(MEA)$_2$ exhibits bands at 421.0, 367.4, 337.5, 308.5 and 290.7 cm^{-1} all of which are shifted to lower frequencies by the ^{104}Pd—^{110}Pd isotopic substitution. The 290.7 cm^{-1} band may be assigned to the bending mode (B) which corresponds to the 282 cm^{-1} band of Ni(MMEA)$_2$. Among the four remaining bands, two bands at 421.0 and 308.5 cm^{-1} are weaker than those at 367.4 and 337.5 cm^{-1}. Furthermore, the former two bands give larger shifts than the latter two bands when the NH$_2$ hydrogens of the MEA ligand are deuterated (Table II). Therefore, they are reasonably assigned to the modes predominantly due to the Pd—N stretching modes. Then, the bands at 367.5 and 337.5 cm^{-1} are assigned to the Pd—S stretching modes.

^{58}Ni(MEA)$_2$ exhibits four metal-isotope sensitive bands in the 450-200 cm^{-1} region. They are at 377.1, 336.1, 330.1, and 291.9 cm^{-1}. The last band may be assigned to the bending mode (B) which corresponds to the 290.7 cm^{-1} band of Pd(MEA)$_2$. Among the three remaining bands, the bands at 377.1 and 330.1 cm^{-1} show very little shifts by the deuteration of the NH$_2$ hydrogens. Therefore, they have been assigned to the Ni—S stretching modes. The 336.1 cm^{-1} band gives a shift of 8.6 cm^{-1} by the same deuteration, and is reasonably assigned to the Ni—N stretching mode. Then, it is most reasonable to assume that another weak Ni—N stretching band is hidden under the 377.1 cm^{-1} band in this case.

^{58}Ni(MPA)$_2$ exhibits five bands at 385.5, 354.7, 312.0, 277.5, and 229.2 cm^{-1} which are sensitive to the ^{58}Ni—^{62}Ni substitution. Again, the last band at 229.2 cm^{-1} may be attributed to the bending mode (B) of the six-membered chelate ring which corresponds to the 290 cm^{-1} band of the MEA complexes. Among the remaining four bands, two bands at 385.5 and 354.7 cm^{-1} give large shifts (12.5 and 8.7 cm^{-1}, respectively) relative to others when the NH$_2$ group is deuterated. Therefore, they are reasonably assigned to the Ni—N stretching modes. Then, the bands at 312.0 and 277.5 cm^{-1} must be assigned to the Ni—S stretching modes.

As stated previously, the *trans* complex exhibits three bending modes, A, B and C. Table II shows that the *cis* complex also exhibits these three modes and that A and C each split into two bands. According to the results of normal coordinate analysis on the [Pd(en)$_2$]$^{2+}$ ion,[17] the non-planar chelate ring of ethylenediamine exhibits at least three bending modes

Table III. M-S Stretching Frequencies of Square-planar NiL_2 and PdL_2 Type Complexes (cm^{-1}).

L or L^-	Ni^{II}	Pd^{II}	Reference
MEA(*cis*)	377.1	376.4	This work
	330.1	337.0	
MMEA(*trans*)	397.3	367.0	This work
Methyldithiene	435	448	12
	333	337	
Phenyldithiene	465	—	12
	449	—	
3-Mercapto-1,3-diphenyl-prop-2-en-one	395	393	10
Dithioacetylacetonate	390	366	11
	371		
Dithiooxalate	435	430	6
	420	420	
Dithiocarbamate	385	387	4
Ethylxanthate	383	362	5
	360	330	

Table IV. Absorption Maxima of Electronic Spectra of NiN_2O_2 and NiN_2S_2 Type Complexes in the Solid State (10^3 cm^{-1})

Ni(sal-me-imine)$_2$ [a]	Ni(3-OCH$_3$-sal-en) [b]	Ni(MMEA)$_2$	Ni(MEA)$_2$	Ni(MPA)$_2$
trans-NiN_2O_2	*cis*-NiN_2O_2	*trans*-NiN_2S_2	*cis*-NiN_2S_2	*cis*-NiN_2S_2
		29.4	30.8	30.8
21.2	—	25.5(shoulder)	26.5(shoulder)	27.0
16.9	17.9	20.3(19.86) [c]	21.4	21.0
—	13.5	14.0(14.06) [c]	16.2	16.2

[a] Sal-me-imine: N-methylsalicylaldimine (Ref. 20). [b] 3-OCH$_3$-sal-en: 3-methoxy-salicylaldehydeethylenediimine (Ref. 20). [c] Value in $CHCl_3$ solution.

at *ca.* 580 (A), 280 (B) and 175 cm^{-1} (C). These three bands are also observed for the *tran*–$[Co(en)_2Cl_2]^{2+}$ ion[17] and $Ni(DTH)_2X_2$ where DTH is 2,5-dithiahexane.[18] As seen in Table II, the A band shows a relatively small shift by the metal isotope substitution and a large shift by the deuteration of the NH_2 group. Therefore, it must be a ring deformation coupled strongly with the NH_2 rocking mode. The frequency of the B band is also slightly sensitive to the metal isotope substitution and markedly sensitive to the NH_2 deuteration. However, this band does not split into two bands in the *cis* complex. It is probably due to a vibration mainly involving the change in the N–M–S angle inside the chelate ring. The frequency of this mode decreases drastically in going from the five-membered (MEA complex) to six-membered (MPA complex) ring because the repulsive force between the nitrogen and sulfur atoms decreases markedly. The C band is insensitive to either substitution and splits into two bands in the *cis* complex. It is most reasonable to assign it to the bending mode involving the central angles between two chelate rings; the N–M–S angle in the *trans* and the N–M–N and S–M–S angles in the *cis* complex. As is seen in Table II, the *cis* complex exhibits two C bands at 167-155 and 154-139 cm^{-1}; the latter probably corresponds to the N–M–N angle bending since it is more sensitive to the NH_2 deuteration than the former.

Ni–S and Pd–S Stretching Frequencies. Table III compares the Ni–S and Pd–S stretching of square-planar NiL_2 and PdL_2 (L: a chelate ligand) type complexes thus far reported. It is seen that these frequencies are in the range of 470-330 cm^{-1} and that the Ni–S and Pd–S stretching frequencies do not differ appreciably if the ligand is the same. Except the MEA and MMEA complexes studied here, all the complexes listed form planar chelate rings. Furthermore, the M–S stretching frequencies of all the complexes forming four- or six-membered π-coniugated chelate rings are similar to those of the MEA and MMEA complexes (below 400 cm^{-1}), whereas those of methyldithiene, phenyldithiene and dithiooxalato complexes which form five-membered rings are much higher than those of other complexes. In agreement wit Schrauzer,[19] this result may indicate that the M–S bond of the odd-membered ring is stronger than that of the even-membered ring because the delocalized π system including the metal ion can be formed only in the former.

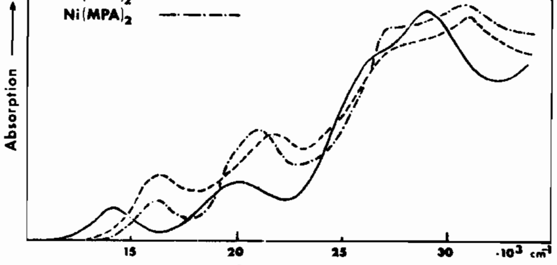

Figure 3. Electronic spectra of Ni(MMEA)$_2$, Ni(MEA)$_2$ and Ni(MPA)$_2$ in the solid state.

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Electronic Spectra

The *cis* and *trans* configurations of square-planar Ni^{II} complexes can be distinguished by the *d–d* transition. Maki[20] has shown from crystal field theory that a *trans*-square-planar complex such as Ni(sal-me-imine)$_2$ absorbs at lower energies than a *cis*-square-planar complex such as Ni(3–OCH_3–sal–en)$_2$ (for abbreviation see Table IV). The same trend is expected to hold for the present case since the crystal field splitting parameter of the S^- donor is almost the same as that of the O donor. Figure 3 and Table IV show that all the four transitions of Ni(MMEA)$_2$ are at lower energies than those of the corresponding transitions of Ni(MEA)$_2$ and Ni(MPA)$_2$. Therefore, the electronic spectra also support the conclusions obtained from the far-infrared study. The Pd^{II} complexes exhibit only one strong band with shoulders on the lower energy side because the change-transfer bands are overlapped on the *d–d* transitions. It was not possible, therefore, to obtain structural information on the Pd complexes from their electronic spectra.

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