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Nickel(II) Complexes of *N*,*N*′-Polymethylenebis(*o*-mercaptobenzylamine)

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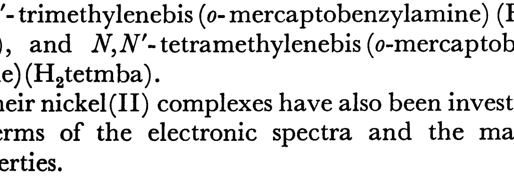
N,*N*′-Polymethylenebis(*o*-mercaptobenzylamine) ligands (polymethylene=ethylene, 1,2-cyclohexylene, trimethylene, and tetramethylene) have been synthesized by the reduction of the corresponding amides, which were prepared by the condensation of 2,2′-dithiodibenzoyl chloride and polymethylenediamines, and then their nickel(II) complexes have been prepared and characterized. The elemental analyses and the magnetic and spectroscopic data indicate that all of the complexes are monomeric with metal-ligand ratio of 1:1, and their geometries are essentially square-planar. When the bridging carbon chain was replaced from ethylene up to tetramethylene, the electronic spectra of the complexes exhibited pronounced change in the d-d bands.

As a typical N_2O_2 type quadridentate ligand, *N*,*N*′-ethylenebis(salicylideneimine)(salen) is well known to form square-planar complexes with nickel(II) ions as well as other transition metal ions.[1] A sulfur analogue of salen, *i.e.*, *N*,*N*′-ethylenebis(*o*-mercaptobenzylideneimine)(tib-en), has been synthesized and it acts as a N_2S_2 type quadridentate ligand and also forms a square-planar nickel(II) complex.[2] Both nickel(II) complexes are monomeric in solution, and no significant difference has been observed in their electronic spectra showing only one absorption band due to d-d transition at 18300 cm^{-1} for salen[3] and near 15000 cm^{-1} for tib-en.[2]

O'Connor and West[4] investigated a nickel(II) complex with the hydrogenated ligand of salen, *i.e.*, *N*,*N*′-ethylenebis(*o*-hydroxybenzylamine), and suggested a polymeric structure in which the donor atoms displayed a distorted octahedral arrangement around the nickel ion. This was evidenced by the paramagnetic property and the spectroscopic observation. In this connection it is worthwhile to investigate the hydrogenated ligand of tib-en, *i.e.*, *N*,*N*′-ethylenebis(*o*-mercaptobenzylamine) (H_2enmba), for complex formation with nickel(II) ions.



H_2Xmba

This paper deals with the synthesis of H_2enmba as well as its polymethylene analogues such as *N*,*N*′-1,2-cyclohexylenebis(*o*-mercaptobenzylamine)(H_2chmba), *N*,*N*′-trimethylenebis(*o*-mercaptobenzylamine) (H_2-trimba), and *N*,*N*′-tetramethylenebis(*o*-mercaptobenzylamine)(H_2tetmba).

Their nickel(II) complexes have also been investigated in terms of the electronic spectra and the magnetic properties.

Experimental

Synthesis of the Ligands. To a solution of 2,2′-dithiodibenzoyl chloride (0.01 mol) in 60 ml of dry dioxane was added dropwise a mixture of polymethylenediamine (0.01 mol) and triethylamine (0.02 mol) in dry dioxane (10 ml). The mixture was stirred in an ice-cold water bath for one hour and the resulting precipitate was filtered and quickly washed with cold water. The product was crushed with a glass rod in a large amount of 1% acetic acid until it became nonsticky powder, and filtered, washed with water repeatedly, and dried at 60 °C.

Under a nitrogen stream the powdered polyamide (3 g) was added little by little to a stirred suspension of lithium aluminium hydride (3 g) in 120 ml of dry tetrahydrofuran at room temperature.

After the addition, the stirring was continued for 7 h and 10 ml of cold water carefully added to the mixture with cooling in an ice-bath and then 150 ml of 3 M hydrochloric acid was added. After stirring overnight, the tetrahydrofuran was removed under reduced pressure. The residual solution was allowed to stand in a refrigerator to separate the desired compound as a hydrochloride; it was filtered and washed with a small amount of cold water and acetone. These compounds were pure enough without recrystallization, and the analyses are listed in Table 1 together with the yields and the melting points.

Synthesis of the Nickel(II) Complexes. All of the nickel(II) complexes were prepared in a similar manner. The synthesis of Ni(tetmba) is given as an example: In a warm solution of 15 ml of 65% aqueous ethanol containing sodium hydroxide (0.004 mol), *N*,*N*′-tetramethylenebis(*o*-mercaptobenzylamine) dihydrochloride (0.001 mol) was dissolved. To this was added nickel(II) acetate tetrahydrate (0.001 mol) in 10 ml of water. Formation of a reddish-violet precipitate completed in a few minutes; it was collected by filtration and washed with water. The crude complex was dissolved in DMSO and recrystallized by adding water to give reddish-violet crystals.

Other complexes were purified in the following manner: Ni(enmba) was dissolved in a mixture of chloroform–DMSO (5:8 V/V) and the solution was permitted to stand at room temperature until chloroform had evaporated spontaneously and dark reddish-violet prisms separated. Ni(chmba) and Ni(trimba) were recrystallized from DMF and from a mixture of chloroform–ethanol (2:1 V/V) to give dark reddish-violet needles and blue-violet crystals respectively.

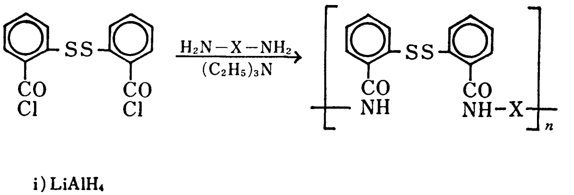
The elemental analyses are listed in Table 2.

Measurements. The molecular weights were determined on a Hitachi Osmometer Type-115 using DMF as a solvent. Electronic spectra were recorded in DMF with a Hitachi EPS-3T spectrophotometer.

A reflectance attachment was used for the measurement of the solid samples. Magnetic susceptibilities were measured by the Gouy method at room temperature and the susceptibilities of the ligand molecules were calculated using Pascal's constants.

Results and Discussion

The ligands may be prepared by the catalytic hydrogenation of corresponding Schiff bases of *o*-mercaptobenzaldehyde with polymethylenediamine, but sulfur poisoning of the catalyst may cause a poor yield of the products. In this case, reduction of a corresponding amide will be more preferable and we found that the following synthetic route gave a fairly good yield to obtain a series of *o*-mercaptobenzylamine bridged by a polymethylene chain.



The condensation of 2,2′-dithiodibenzoyl chloride with polymethylenediamine afforded polymeric amides. The elemental analyses of the amides were in agreement with the unit molecular formulas within an error of 1.9 for carbon, 0.3 for hydrogen, and 0.9 for nitrogen percentages. The amide carbonyl and the disulfide bond underwent reduction simultaneously with lithium aluminium hydride and the desired mercaptobenzylamine derivatives were finally isolated as hydrochlorides.

The infrared spectra of these compounds may exhibit absorptions due to a SH stretching vibration in the vicinity of 2550 cm^{-1}. However, these bands were not detected probably due to overlapping with the strong ammonium absorption which appeared in the same region. The nickel(II) complexes are insoluble in water, slightly soluble in most organic solvents, and moderately soluble in *N*,*N*′-dimethylformamide (DMF). Data for the elemental analyses and the molecular weight determination in DMF are listed in Table 2. They indicate that all complexes are monomeric and the ligands act as N_2S_2 type quadridentate dianions.

The electronic spectra of the complexes in DMF exhibit three bands in visible and near-ultraviolet regions as seen in Fig. 1.

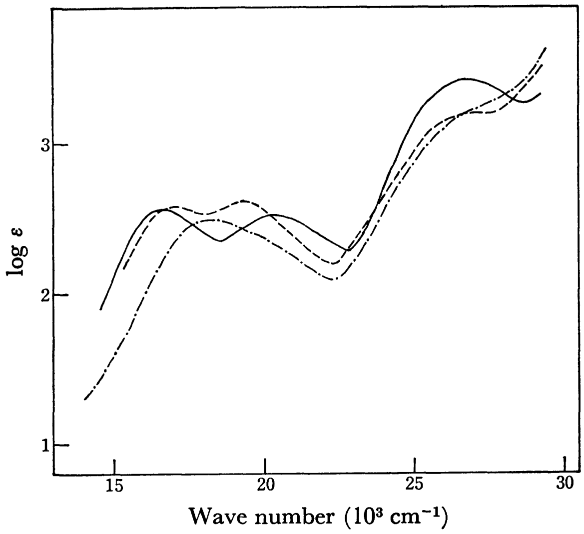


Fig. 1. Absorption spectra of Ni(enmba), ——; Ni(trimba), - - - -; Ni(tetmba), - · -.

The absorption maxima in 10^3 cm^{-1} are: Ni(enmba), 16.7(ε 362), 20.2(ε 319), 26.8(ε 2380); Ni(chmba), 16.8(ε 248), 20.6(ε 301), 27.0(ε 1654); Ni(trimba), 17.0(ε 374), 19.2(ε 405), 27.0(ε 1542); Ni(tetmba), 18.1(ε 309), 19.6sh(ε 258), 27.8sh(ε 1974).

The first and the second low energy bands having a moderate molar extinctions are attributed to d–d transitions, and the third bands in the near-ultraviolet region will be due to charge transfer considering from their high molar extinctions. These spectral patterns are different from that of the nickel(II) complex of tib-en[2] which exhibits only one band near 15000 cm^{-1} in the visible region, but similar to those of square-planar nickel(II) complexes of bis(*N*-substituted 2-aminoethanethiol) which consist of three bands around 16000 cm^{-1} and 20000 cm^{-1} in the visible and 27000—30000 cm^{-1} in the near-ultraviolet regions.[5]

The magnetic susceptibilities of the complexes are very low with magnetic moments of 0.18 B.M. for

Table 1. Analyses, yields, and melting points of the ligands

Ligand	Found (%)			Calcd (%)			Yield (%)	Mp (°C)
	C	H	N	C	H	N		
H_2enmba·2HCl	50.81	6.09	7.38	50.92	5.88	7.42	83	233
H_2chmba·2HCl	55.89	6.49	6.40	55.67	6.54	6.49	34	218—219
H_2trimba·2HCl·$2H_2O$	48.16	6.46	6.50	47.77	6.60	6.55	41	172—177
H_2tetmba·2HCl	53.18	6.44	6.73	53.32	6.46	6.91	40	221—224

Table 2. Analyses and molecular weight data of the complexes

Complex	Found (%)			Calcd (%)			Molecular weight Found(Calcd)
	C	H	N	C	H	N	
Ni(enmba)	53.31	5.05	7.61	53.21	5.02	7.76	422(361)
Ni(chmba)	57.61	5.85	6.73	57.85	5.83	6.75	
Ni(trimba)	53.84	5.33	7.28	54.42	5.37	7.47	406(375)
Ni(tetmba)	55.38	5.80	6.92	55.54	5.70	7.20	358(389)

Ni(enmba), 0.47 B.M. for Ni(chmba), 0.64 B.M. for Ni(trimba), and 0.41 B.M. for Ni(tetmba) at room temperature. These values are often observed for spin-paired ions,[6] and for the d^8 electron configuration of nickel(II), diamagnetism commonly means that the metal ion is coordinated with four strong donor atoms in a square-planar structure or with five donor atoms of phosphorus, arsenic, or sulfur in a trigonal bipyramidal or square-pyramidal structure.

Judging from the spectral similarity with known square-planar nickel(II) complexes with similar N_2S_2 type ligands which consist of a thiol sulfur and a secondary amine nitrogen, five-coordinate structure can be ruled out, and it is concluded that these nickel(II) complexes are essentially square-planar.

It should be noted as pointed out by Gerlach and Holm[7] that substitution of two or more oxygen atoms by sulfur without any other stereochemically significant alternations in ligand composition causes depolymerization of metal complexes. The present case is a typical example which is in conformity with this criterion, namely the nickel(II) complex of *N,N'*-ethylenebis(*o*-hydroxybenzylamine) is polymeric, whereas its mercapto analogues are monomeric.

As for the effect of increasing length of the bridging carbon chain in the diamine moiety, a significant change of the d-d transition bands has been observed in their electronic spectra. When the bridging ethylene was replaced by the trimethylene, the first band moved to a higher frequency, whereas the second one shifted to a lower frequency. In the case of the tetramethylene analogue, two bands almost overlapped at 18000 cm^{-1}.

From the steric consideration, increasing length of the bridging carbon chain will cause the weakening of the ligand field strength and distortion from planarity. Thus in the nickel(II) complexes of *N,N'*-polymethylenebis(salicylideneimine), red shift of the d-d bands with increasing chain length of the polymethylene bridge has been observed.[8] In the present case, the lowest energy bands undergo blue shift with increasing the number of bridged carbon atoms. The source of this phenomenon is not clear at present.

The reflectance spectrum of each complex is essentially similar to the corresponding spectrum in solution, except that a very weak band can be observed around 8000—11000 cm^{-1} in every complex in the solid state. Similar weak absorptions have been observed in the electronic spectra of dithiocarbazatonickel(II) and dithiocarbamatonickel(II) in the solid state and in concentrated solutions, and tentatively assigned to the spin-forbidden $^1A_{1g} \rightarrow {}^3B_{2g}(D_{4h})$ transition.[9] Nevertheless, the possibility of the presence of a small amount of high-spin species together with the predominant low-spin species could not be ruled out.

For the definite assignment, further investigations should be awaited.

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