

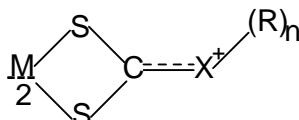
Synthesis and Characterization of Pyridine Adducts of Some Transition Metal 4-Methylpiperazine-1-carbodithioic Acid Complexes

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INTRODUCTION

Often metal complexes expand their coordination number by interaction with a Lewis base. This may take place by intermolecular association or by adduct formation with solvent or available ligands of comparable ligating ability. The physical properties of the resulting complex often are significantly different from those of the complex not having the expanded coordination number. MS_4 ($M = Ni$) complexes vary substantially in their ability to interact with Lewis bases.¹ The ability to interact with bases seems to be related closely to the electronic properties of the ligands as a whole, not just the atoms bonded to the metal.

Infrared studies indicate that structure which contains a polar C-X bond is

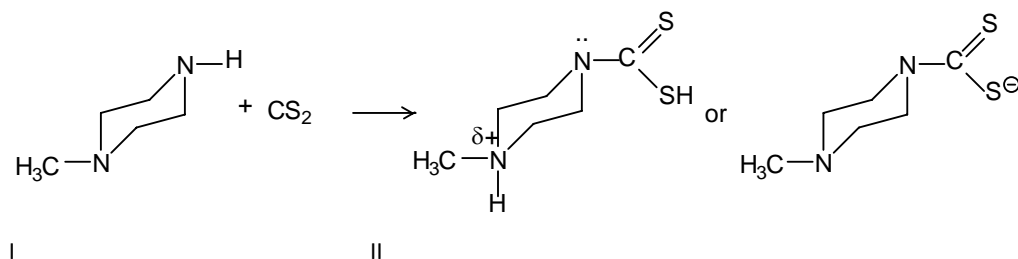


relatively more important in metal dithiocarbamate complexes than in metal xanthates, the relatively lower tendency of dithiocarbamate complexes towards adduct formation with Lewis bases as compared to xanthate complexes is not difficult to understand. If there is difference between the metal dithiocarbamate and the metal xanthate complexes, it may be due to the greater mesomeric electron-releasing tendency of the $-NR_2$ group in dithiocarbamates compared to the $-OR$ group in xanthates. The

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consequent larger charge on sulfur atoms may facilitate greater donation of electron density from the ligating sulfur atoms to non-bonding molecular orbital ($4p_z$ of the metal) in $M^{II}(R_2dth)_2$, thereby decreasing its availability for axial interaction with bases. This factor has been earlier considered responsible for the inability of $Ni(R_2dth)_2$ to form adducts with Lewis bases.² Recently³ the addition of a bidentate amine such as *o*-phenanthroline to dithiocarbamate nickel(II) has been found to involve the moving of the dithiocarbamate from its position in the plane to an edge of the octahedron. This octahedral complex resembles the intermediate of the substitution reaction of square-planar complexes and, in this perspective, merits additional interest.⁴ Mononuclear⁵⁻⁷ and binuclear^{8,9} Lewis base adducts are known for the cadmium bis(dithiocarbamates) for which coordination geometries vary from octahedral^{5,6} to trigonal prismatic⁷ for diamine adducts, and trigonal bipyramidal⁸ to square pyramidal¹⁰ for phosphine adducts.¹¹ The adduct chemistry of zinc⁹ and cadmium¹¹ 1,1-dithiolates have been explored. More recently the polymeric structures of $[M(S_2CO^iPr)_2(4,4-bipy)]_\infty$ ($M = Zn, Cd$)^{12,13} have been reported. Sterically hindered diamine, 2,9-dimethyl-1,10-phenanthroline results in formation of adduct having distorted tetrahedral geometry for bis-(N,N-pyrrolidinedithiocarbamate)zinc(II) showing monodentate binding of dithiocarbamate ligands.¹⁴ Seven novel 2,2'-bipyridine adducts of bis[N,N-dialkylcarbodithioato-S,S']zinc(II) have been synthesized and characterized.¹⁵ Thus, in the dithiocarbamates, the type of R-group in the $-NR_2$ moiety is expected to influence the stability and other physico-chemical properties of a metal complex, depending on the inductive effect of the group(s) attached to the nitrogen atom. There has, therefore, been considerable interest in recent years in the preparation of dithio-complexes in which the R-group has been varied over a wide range. Considering the wide spread interest in metal dithiocarbamate complexes on one hand and in the mechanism of additions to square planar/tetrahedral metal complexes on the other hand, it has been considered of interest to attempt such a study of addition products of metal carbodithioate complexes. Herein, 1-methylpiperazine (I), a saturated heterocyclic secondary amine has been used to obtain carbodithioic acid, 4-MPipzcdth (II).



EXPERIMENTAL

MATERIALS AND METHODS

All the chemicals used were of analytical reagent grade and used as such. The ligand 4-methylpiperazine-1-carbodithioic acid (4-MPipzcdtH) and its zwitterionic complexes $[M(4-MPipzcdtH)_2](X)_2$ were prepared by the method as reported earlier.^{16,17}

Preparation of $[M(4-MPipzcdtH)_2]X_2$ (M = Co(II), Ni(II), Cu(II) and Zn(II) where X = ClO₄ and M = Co(II), Zn(II), Cd(II), Hg(II) where X = Cl)

Slightly less than stoichiometric amount of the solid 4-methylpiperazine-1-carbodithioic acid (0.100g; 0.568 mmol) was added in small portions (~10 mg) after successive intervals of 10 minutes in a total period of one and half an hour to a continuously stirred ethanolic solution (3 ml) of 0.284 mmol of $MX_2 \cdot xH_2O$ (M = Zn(II) and X = ClO₄ when x = 6; M = Zn(II), Hg(II) and X = Cl when x = 0; M = Cd(II) and X = Cl when x = 1). Green for cobalt(II) and nickel(II), brown for copper(II) and white to cream coloured precipitate of the complex separated as the solid carbodithioic acid dissolved. It was then filtered and dried in air. All the complexes have been characterized in detail and reported elsewhere.¹⁶⁻¹⁷

PREPARATION OF PYRIDINE ADDUCTS

$[M(4-MPipzcdtH)_2(Py)_2](ClO_4)_2$ (M = Co(II), Ni(II), Cu(II), Zn(II)):

To methanolic solution of $[M(4-MPipzcdtH)_2](ClO_4)_2$ (M = Co(II), Ni(II), Cu(II), Zn(II)) (0.385g; 0.626 mmol) was added with stirring slightly more than the stoichiometric amount (1.38 mmol) of pyridine solution in methanol (5 ml). The stirring was continued for another one hour when the intense coloured solutions of the complexes of the Lewis base were obtained except in case of copper(II) complex. The solution of the adduct was filtered quickly so as to remove any impurity. The solvent from solution of the complexes was allowed to evaporate slowly in air when granular solid products were obtained. In the case of pyridine adduct of $[Cu(4-MPipzcdtH)_2](ClO_4)_2$ complex, solid brown coloured product was obtained which was filtered, washed with methanol and dried in air.

$[M(4-MPipzcdtH)_2(Py)_2]Cl_2$ (M = Co(II), Zn(II), Cd(II), Hg(II)):

To the solution of pyridine (0.110g; 1.38 mmol) in methanol was added solid sample (0.626 mmol) of $[M(4-MPipzcdtH)_2]Cl_2$ (M = Co(II), Zn(II), Cd(II), Hg(II)) in small portions (~10 mg) after successive intervals of five minutes in a total period of five hours. The reaction mixture was further stirred for

another one hour when the pyridine adducts of the complexes were obtained in solution state. Solid complexes were obtained after evaporating the solvent in air.

ELEMENTAL ANALYSES

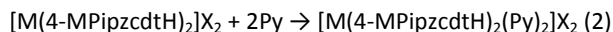
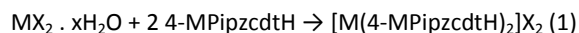
Carbon and hydrogen analyses were performed on an automatic Coleman-33 analyzer, while nitrogen was determined by Kjeldahl's method. Cobalt, nickel, copper, cadmium, zinc and mercury contents in the complexes were determined volumetrically by EDTA titration using Xylenol orange; Eriochrome Black T as indicators. Chloride content was estimated volumetrically by mercuric nitrate titration using diphenylcarbazone indicator and sulfur was determined gravimetrically as barium sulfate.

PHYSICAL MEASUREMENTS

Infrared spectra of pyridine adducts were recorded as KBr pellets on Nicolet 5700 FT Infrared Spectrophotometer in the 4000-600 cm^{-1} region while as nujol mull with cesium chloride plates as windows in the 600-200 cm^{-1} region. Solution (DMSO) electronic absorption spectra of the complexes, with the solvent as the reference, in quartz glass cells were recorded on Cary 100 Bio UV-Visible recording Spectrophotometer (range 200-900 nm) and Analytikjena Specord 200 UV-Visible recording Spectrophotometer. Molar conductances (10^{-3} M solutions in DMSO) were obtained at 25 ± 0.1 °C using a type Elico Conductivity Bridge CM-82T. The cell constant of the conductivity cell was 0.4530 cm^{-1} . Room temperature magnetic susceptibility measurements for the complexes were made on finally powdered samples using Gouy method. Variable temperature magnetic susceptibilities of two of the samples were measured on a Vibrating Sample Magnetometer PAR-155 with variable temperature cryostat (model-152).

RESULTS AND DISCUSSION

Preparation of complexes, $[\text{M}(\text{4-MPipzcdtH})_2]\text{X}_2$ (M = Co(II), Ni(II), Cu(II), Zn(II) and X = ClO_4 ; M = Co(II), Zn(II), Cd(II), Hg(II) and X = Cl) follow the general reaction (1). The synthesis of pyridine adducts of $[\text{M}(\text{4-MPipzcdtH})_2](\text{X})_2$ to yield complexes of the corresponding general formula $[\text{M}(\text{4-MPipzcdtH})_2](\text{Py})_2\text{X}_2$ based on elemental analyses has been described by the Eq. (2).



Py = Pyridine

M = Co(II), Ni(II), Cu(II), Zn(II) when X = ClO_4

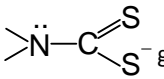
M = Co(II), Zn(II), Cd(II), Hg(II) when X = Cl

Pyridine adducts of metal carbodithioic acid complexes are soluble in DMSO but have no solubility in other common organic solvents. The coloured complexes are of high stability and high purity. The adducts do not melt but decompose between 140-320 °C.

IR SPECTRA

A shift in $\nu(\text{C}=\text{N})$ values to lower wave numbers (34-54 cm^{-1}) in complexes of pyridine adducts with metal 4-methylpiperazine-1-carbodithioic acid complexes as compared to corresponding parent metal 4-methylpiperazine-1-carbodithioic acid complexes (1493-1465 cm^{-1})^{16,17} has been observed. This shift towards lower wave numbers has been ascribed to change in coordination number from 4 to 6 with change in geometry from tetrahedral/square planar to octahedral. This is in consonance with the probable arrangement of sulfurs around the central atom in the following decreasing order:¹⁸

planar > tetrahedral > octahedral > distorted octahedral

The reduction in $\text{C}=\text{N}$ stretching frequency in the pyridine adducts arises because of the relatively decreased electron flow of the nitrogen lone pair of electrons of  group towards the central metal ion. Since the central metal ion also receives additional electron density from the two new pyridine ligands resulting into adduct formation.

Two bands have been observed in the region 993-969 cm^{-1} for the antisymmetric, $\nu_a(\text{SCS})$ vibration indicating unsymmetrical binding of the chelating agents. As expected the CS_2 symmetric stretch is slightly affected on complexation and is observed in the region 698-683 cm^{-1} .

The absence of the $\nu(\text{Cl-O})$ band at 920 cm^{-1} supports the ionic nature of the perchlorate group.¹⁹ The band around 1087-1083 cm^{-1} is assigned to the ν_3 vibration of the ionic perchlorate of T_d symmetry. Also the observation of another band around 627-625 cm^{-1} due to the ν_4 vibration of the perchlorate group supports the ionic nature of the group. The skeletal ring breathing modes of pyridine appear as four strong and sharp bands at 1602, 1581, 1482 and 1440 cm^{-1} in free pyridine. In the pyridine adducts of metal carbodithioic acid complexes with perchlorate or chloride as counter anions of the present study, all the four bands of free pyridine are considerably blue shifted around 1638-1606, 1599-1583, 1487-1483 and 1474-1463 cm^{-1} indicating coordination of pyridine through the nitrogen atom in adduct formation with metal carbodithioic acid complexes. The blue shift in the pyridine stretching is due to back-bonding from metal to the pyridine ring through formation of extensive π -bonding.

The appearance of additional band in the 355-320 cm^{-1} region as compared to free 4-MPipzcdtH ligand²⁰⁻²⁷ reveals the formation of metal-sulfur bonds and hence is ascribed to their stretching M-S vibrational modes. The M-N band appears at about (262-223 cm^{-1}) in the pyridine adducts of present study.

MOLAR CONDUCTANCE STUDIES

The DMSO solutions of pyridine adducts of the general formulae $[\text{M}(\text{4-MPipzcdtH})_2(\text{Py})_2](\text{ClO}_4)_2$ (M = Co(II), Ni(II), Cu(II), Zn(II)) and $[\text{M}(\text{4-MPipzcdtH})_2(\text{Py})_2]\text{Cl}_2$ (M = Co(II), Zn(II), Cd(II), Hg(II)) exhibit molar conductance values between 168-179 $\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$, which is indicative of 1:2 electrolytic nature of the complexes.²⁸

MAGNETIC AND ELECTRONIC ABSORPTION SPECTRAL STUDIES

For the complexes, viz. $[\text{Co}(\text{4-MPipzcdtH})_2(\text{Py})_2](\text{ClO}_4)_2$ and $[\text{Co}(\text{4-MPipzcdtH})_2(\text{Py})_2]\text{Cl}_2$, the room-temperature magnetic susceptibility measurements give μ_{eff} values of 1.86 and 1.84 B.M. respectively which lie in the range of the values for low-spin octahedral cobalt(II), d^7 complexes (1.70-1.85 B.M.).²⁹ The magnetic data thus suggest ${}^2A_{1g}$ as the ground state for the complexes with $[\text{CoN}_2\text{S}_4]$ chromophore. The electronic absorption spectra of these complexes, viz. $[\text{Co}(\text{4-MPipzcdtH})_2(\text{Py})_2](\text{ClO}_4)_2$ and $[\text{Co}(\text{4-MPipzcdtH})_2(\text{Py})_2]\text{Cl}_2$, exhibit three well defined bands. The lowest energy band around 11,408-11,484 cm^{-1} is a weak band and has been assigned to spin forbidden / spin allowed transition. The second and third bands of high intensity falling in the regions 15,049 -15,649 and 20,686 - 20,703 cm^{-1} are assigned to 2E_g (${}^2T_{2g}$) \leftarrow ${}^2A_{1g}$ and (components of ${}^2T_{1g}$) \leftarrow ${}^2A_{1g}$ transitions respectively for an axially elongated low spin octahedral configuration.³⁰

The room-temperature μ_{eff} value for $[\text{Ni}(\text{4-MPipzcdtH})_2(\text{Py})_2](\text{ClO}_4)_2$ is 2.93 B.M. and has been found to be independent of temperature between 80-296.5 K revealing an octahedral stereochemistry with ${}^3A_{2g}$ as the ground term. In the DMSO solution electronic absorption spectrum of the complex three bands have been observed and lie at 11,574, 15,082 and 25,316 cm^{-1} . In view of the nature of the chromophore, i.e. $[\text{NiS}_4\text{N}_2]$ for the complex $[\text{Ni}(\text{4-MPipzcdtH})_2(\text{Py})_2](\text{ClO}_4)_2$, the lowest energy band is assigned to the transition (ν_1) (components of ${}^3T_{2g}$) ${}^3B_{2g}$, ${}^3E_g \leftarrow$ (${}^3A_{2g}$) ${}^3B_{1g}$, the middle energy band to the transition (ν_2) ${}^3T_{1g}(\text{F}) \leftarrow$ ${}^3A_{2g}$ and higher energy band has been assigned to the transition (ν_3) ${}^3T_{1g}(\text{P}) \leftarrow$ ${}^3A_{2g}$. The extent of splitting of the ν_1 band into two components of the order of 2087 cm^{-1} infers a *trans*- NiS_4N_2 tetragonally distorted octahedral structure of D_{4h} symmetry.³¹

For the pyridine adduct $[\text{Cu}(\text{4-MPipzcdtH})_2(\text{Py})_2](\text{ClO}_4)_2$ having $[\text{CuS}_4\text{N}_2]$ chromophore, the room temperature μ_{eff} value (1.91 B.M.) which has been found to be independent of temperature between 296.5 to 80 K, correspond to octahedral structure.

For the complex three energy bands have been observed around 13,386, 18,446 and 22,883 cm^{-1} in its DMSO solution electronic absorption spectrum. The lower energy band assigned to the transition $x^2-y^2 \leftarrow z^2$ is of low intensity, the middle energy band is a relatively broad band assigned to the transition $x^2-y^2 \leftarrow xy$ and the highest energy band of medium intensity is ascribable to the transition $x^2-y^2 \leftarrow xz, yz$. The third high energy band is a sharp band of very high intensity and sometimes shows a sign of splitting too. The assignment of bands corresponds to a six-coordinate tetragonal copper(II) complex.³⁰

The adducts, viz. $[\text{Zn}(4\text{-MPipzcdtH})_2(\text{Py})_2](\text{ClO}_4)_2$, $[\text{Zn}(4\text{-MPipzcdtH})_2(\text{Py})_2]\text{Cl}_2$, $[\text{Cd}(4\text{-MPipzcdtH})_2(\text{Py})_2]\text{Cl}_2$ and $[\text{Hg}(4\text{-MPipzcdtH})_2(\text{Py})_2]\text{Cl}_2$ are all diamagnetic (0.22-0.28 B.M.) and their DMSO solution electronic absorption spectra exhibit bands around 18,446-22,411, 22,552-27,624 and 35385-37313 cm^{-1} .³¹

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