TRANSITION METAL BIS(2-BROMOPHENYL)DISULFIDE COMPLEXES

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ABSTRACT

The interactions of the new ligand bis(2-bromophenyl)disulfide ($(\text{BrPh})_2\text{S}_2 = \text{L}$) with transition metal ions are described. Octahedral complexes $[\text{ML}_2\text{Cl}_2(\text{H}_2\text{O})_2]$ ($\text{M} = \text{Mn(II)}, \text{Fe(II)}, \text{Co(II)}$ or Ni(II)) and $[\text{CrL}_2\text{Cl}_2(\text{H}_2\text{O})_2]\text{Cl}$ were obtained and characterized by physicochemical and spectroscopic methods which suggest that the bis(2-bromophenyl)disulfide behaves as a monodentate ligand

Keywords: bis(2-bromophenyl)disulfide, transition metal complexes

INTRODUCTION

During the past years a remarkable series of compounds of transition and main metals have been reported in which the central metal ions have been coordinated by aromatic or insaturated compounds containing sulfur donor atoms. Some papers in the past summarized what is known to date about the electronic and structural properties of the species.¹⁻³ The behaviour of the disulfide group as a donor in transition metal complexes has not been subjected to such detailed study as a number of other donor groups. This arises in part, because the disulfide group often gives metal ion derivatives that are extremely insoluble, bridged, or even polymeric. Further, these substances are easily oxidized and the susceptibility of coordinated disulfide ligands to cleave via oxidative addition is a difficulty inherent in the preparation and isolation of metal disulfide complexes.⁴ However, the theoretical interest and biological importance of them cause that the elucidation of the manner of interaction of this function with metal ions to be of great interest. They potentially could serve as models for biological systems. Binuclear species with bridging sulphur atoms play an important role in active sites of metalloenzymes such as nitrogenase, hydrogenase or CO-dehydrogenase.^{5,6} Furthermore, conversion of thiols to disulfides is important from both biological and synthetic point of view.^{7,8} Dehydroascorbic acid, flavins, cytochromes oxidizes thiols to control the cellular redox potential and prevent oxidative damage in biological systems.⁹⁻¹¹ We report herein the synthesis and characterization of metal complexes containing bis(2-bromophenyl)disulfide as a ligand.

Transition metal bis(2-bromophenyl)disulfide complexes

EXPERIMENTAL

Materials

$\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, ZnCl_2 , HgCl_2 and 2-bromothiobenzene were obtained from Aldrich. All solvents were of analytical reagent grade and were purified by distillation according to the standard methods.

Synthesis of $(\text{BrPh})_2\text{S}_2$ ligand

The free ligand L was obtained when we were attempting to form zinc(II) or mercury(II) complexes with 2-bromophenylmercaptan. Metallic sodium (0.50 g) was added to a solution of 2-bromophenylmercaptan (1 mmol) in methanol (50 mL). Then to the resulting mixture, ZnCl_2 or HgCl_2 (0.5 mmol) was added. The mixture was stirred at room temperature during two days and then the solution was filtered and concentrated to 5 mL. This solution was left standing at room temperature and in a few days, X-ray quality colourless prismatic crystals of the bis(2-bromophenyl)disulfide ligand were obtained.

Synthesis of metal complexes

Metallic sodium (0.50 g) was added to a solution of bis(2-bromophenyl)disulfide (1 mmol) in methanol (50 mL). Then to the resulting mixture, metal chloride salts (0.5 mmol) were added. The mixture was stirred at room temperature during two days after which time a precipitate formed. The products were collected by suction filtration, rinsed with water, methanol and ether and finally dried in a vacuum desiccator over anhydrous CaCl_2 .

Physical methods

Fourier transform infrared (FTIR) spectra of the ligand and its metal complexes as KBr pellets were recorded in the spectral range 4000 - 400 cm^{-1} with a Perkin-Elmer Series 2000 apparatus. FTIR spectra as polyethylene pellets were registered between 450 - 120 cm^{-1} using Bruker IFS 66V spectrophotometer. EPR spectra were recorded on a Bruker ECS 106 spectrometer operating in the X-band (9.76 GHz). α - α' -Diphenyl- β -picrylhydrazide free radical was used as the g marker. U.v.-vis. spectra were recorded using a Perkin-Elmer recording spectrometer. C, H, and S were analyzed on a LECO CHNS 932 model microanalytical instrument. The metal contents in the complexes was determined with a Perkin-Elmer atomic absorption spectrophotometer in solutions prepared by decomposition of the complex in conc. HCl and conc. HNO_3 (3:1) solution followed by dilution in water. Magnetic susceptibilities were measured on a Johnson Matthey susceptibility balance at room temperature using $\text{HgCo}(\text{NCS})_4$ as calibrant. The differential scanning calorimetric (DSC) analysis was measured using a Thermo DSC-Q20 instrument at a heating rate of 4°C min^{-1} up to 200°C.

RESULTS AND DISCUSSION

Colourless crystals of bis(2-bromophenyl)disulfide are obtained from the reaction of 2-bromophenylmercaptan with metallic sodium and either zinc chloride or mercury chloride in methanol. In the presence of zinc(II) ions, the crystals are orthorhombic, whereas with mercury(II) ions present, the product is triclinic.¹² It is concluded that air oxidation of thiol to disulfide was catalyzed by the addition of metal chlorides, may be due to the formation of metal thiolate complex in solution which converts to disulfides upon standing on air for two days. It appears that both metal chlorides sterically control the stereochemistry of disulfides during its conversion from thiol and results in the formation of two different polymorphs with high yields.

Complexation reactions between the ligand and the metal salts were carried out to investigate the coordination capability of the ligand. The complexes were prepared by reaction of the ligand with appropriate metal salts in 2:1 molar ratios in methanol. Stoichiometries and elemental analyses of the metal chelates of bis(2-bromophenyl)disulfide are given in Table 1.

Table 1. Elemental analyses for the complexes

	Found (Calcd.) %			
Compound	C	H	S	Metal
$L = [(C_6H_4Br)_2S_2]$	38.2 (38.3)	2.4 (2.1)	17.2 (17.0)	
$[CrL_2Cl_2(H_2O)_2]Cl$	31.3 (31.6)	1.8 (2.2)	14.4 (14.1)	5.3 (5.7)
$[MnL_2Cl_2(H_2O)_2]$	31.7 (31.5)	1.9 (2.2)	13.7 (14.0)	6.4 (6.0)
$[FeL_2Cl_2(H_2O)_2]$	31.9 (31.5)	1.9 (2.2)	14.3 (14.0)	6.3 (6.1)
$[CoL_2Cl_2(H_2O)_2]$	31.6 (31.4)	2.1 (2.2)	14.1 (14.0)	6.6 (6.4)
$[NiL_2Cl_2(H_2O)_2]$	31.8 (31.4)	2.0 (2.2)	14.4 (14.0)	7.1 (6.4)

Analytical data of these complexes correspond to the formation of mononuclear complexes. The complexes are stable in atmosphere and insoluble in polar and non polar solvents. The insolubility of the complexes suggest that they would be polymeric. In the more solvolysing solvent DMSO the complexes are slightly dissociated but the conductance values of the 10^{-3} M solutions of the metal(II) complexes are still considerably below the value expected for a 1:1 electrolytes,¹³ while that for the chromium(III) complex corresponds to a 1:1 electrolyte. Thus, conductance data suggests that the chloride ion is coordinated to the metal ion. These results may suggest that when corresponding metal salts of noncoordinating anions such as nitrate, acetate and perchlorate are used, different types of complexes could be formed, emphasizing the importance of reaction conditions and type of the anions on the structure of complexes. The present compounds often give metal ion derivatives that are extremely insoluble, bridged or even polymeric. However, if other strong ligands are introduced, polymeric products can often be avoided even under conditions favoring sulfur bridging.

Thermograms of the hydrated metal complexes indicate endothermic decompositions in the 150-160 °C range due to the loss of molecules of coordinated water and also reveal that the complexes are stable with no hydration water and solvent molecules. Because of their low solubilities, no molecular weight determination nor NMR studies were performed on the products. All attempts to form complexes with copper(II), zinc(II), cadmium(II) and mercury(II) ions were unsuccessful, probably due to kinetic effects and/or problems forming a transition state with the less accommodating heavy metal ions.

Vibrational spectra

IR spectroscopy can provide valuable information as to whether or not reaction has occurred. The spectra of the complexes show similarities to one another and reveal the absorptions expected for their structure. The more relevant spectroscopic properties exhibited by the complexes are the appearance of new bands in the 350-395 cm^{-1} range attributed to ν (M-S) vibrations suggesting that the product has been formed and the ν (S-S) stretching mode appreciated in the 660-680 cm^{-1} range showing that not cleavage have occurred. In the latter case, the bands were shifted by 20-30 cm^{-1} to lower energy relative to the free ligand, what can be associated with the coordination of the disulphide group and its incorporation into the chelate ring. The complexes show bands at 1410-1460, 1070-1100 and 740-750 cm^{-1} region which can be assigned to phenyl ring vibrations.¹⁴ A strong band in the 990-1100 cm^{-1} region due to C-S stretching vibrations is suggestive of the chelating character of the ligands in the case of metal complexes.¹⁵ Another C-S stretching mode was observed in the 1240-1320 cm^{-1} region in accordance with the literature.¹⁶ In the same way, a C-Br stretching band can be appreciated at 550-600 cm^{-1} range. However, the ν (M-Cl) could not be unambiguously distinguished. The solid complexes showed IR spectral bands characteristic of coordinated water at 3400-3500 cm^{-1} together with a broad band of moderate intensity at 420-520 cm^{-1} which is usually assigned to wagging or rocking modes of coordinated water.

Electronic and magnetic data

The electronic spectrum in Nujol solution of the chromium(III) complex is expected to show three spin-allowed d-d transitions, viz. $^4A_{2g}(F) \rightarrow ^4T_{2g}(v_1)$, $^4A_{2g} \rightarrow ^4T_{1g}(F)(v_2)$ and $^4A_{2g} \rightarrow ^4T_{1g}(P)(v_3)$. Three bands are observed at 595

(v_1), 470 (v_2) and 360 (v_3) nm suggesting an octahedral geometry around the chromium(III) ion with substantially $^4A_{2g}$ ground state.¹⁷ The manganese(II) complex shows a very weak absorption at 390 nm probably due to a spin-orbit forbidden transition. The electronic spectrum of the cobalt(II) complex gave two bands, corresponding to octahedral geometry of the cobalt(II),^{17,18} which lie in the regions 430 and 400 nm and may reasonably be assigned to the $^4T_{1g}(F) \rightarrow ^4T_{2g}(F)$ and $^4T_{1g}(F) \rightarrow ^4A_{2g}(F)$ transitions, respectively. The uv visible spectrum of the nickel(II) complex in Nujol solution present two major absorptions maxima, at 240 and 350 nm are presumably due to intraligand excitation. There are also d-d bands at 400 and 480 nm which may be assigned, considering that the immediate coordination sphere of the metal is O_h symmetry, to the transitions $^3A_{2g} \rightarrow ^3T_{1g}(P)$ and $^3A_{2g} \rightarrow ^3T_{1g}(F)$ respectively.¹⁹

From the molar magnetic susceptibility values, corrected magnetic moments were calculated using Pascal's constants. The magnetic moment value (3.80 B.M.) for the chromium(III) complex is in agreement with the values reported for octahedral geometry around the chromium(III) ion.²⁰ The room temperature magnetic moment of the iron(II) complex is 4.98 B.M., showing that the iron(II) ion is high spin with an $S = 2$ ground state. The magnetic susceptibility values for Mn(II) and Co(II) were 5.6 and 5.1 B.M., respectively, suggesting an octahedral arrangement around the metal, as compared with the reported values for octahedral complexes of manganese(II) (5.5-6.0 B.M.) and cobalt(II) (4.7-5.2 B.M.).^{21,22} The nickel(II) complex has a magnetic moment of 3.1 BM characteristic of two unpaired electrons and greater than the spin-only value, presumably due to the orbital contribution resulting from the transfer of an electron from the $d_{x^2-y^2}$ orbital to the d_{xy} orbital. The complex therefore probably has distorted octahedral geometry.

The room temperature EPR spectra of the powder sample of the manganese(II) complexes showed a single broad signal with a poor resolution of the hyperfine structure. The calculated g value of 2.03 agrees well with the results obtained previously for high spin manganese(II) complexes.

Structure of complexes

Organic disulfide ligands are able to function in two different coordination modes: as monodentate ligands (terminal or end-on coordination) by using only one of the sulfur atoms (A), and as bidentate ligands (bridging or cis end-on coordination) by using both sulfur atoms (B). In some cases, the M-S bond does not exist. A different coordination mode, i.e. a side-on coordination, where both disulfide sulfur atoms coordinate a metal centre, has not been reported in the literature.^{4,23-25}

Aromatic disulfides containing phenyl group, Ph-S-S-Ph, have scarcely been studied as potential ligands. The complex formulated as $[Ag_2(Ph_2S_2)_4][AsF_6]$ has been synthesized.²⁶ In its structure, the ligand adopts a terminal type A coordination and a bridging type B coordination, this been the first case reported in the literature with these surprising characteristics. Several binuclear complexes contain type B disulfide ligands: $[Pd_2(Ph_2S_2)_2Cl_4]$,²⁷ $[Re_2(CO)_6(Ph_2S_2)Br_2]$,²⁸ $[(CpFe(CO)_2)_2(Ph_2S_2)](PF_6)_2$ and $[(Cp^*Fe(CO)_2)_2(P h_2S_2)](PF_6)_2$ (Cp and Cp* are $[C_5H_5]$ and $[C_5Me_5]$ respectively),²⁹ where a structure with two metal moieties bridged by molecules of Ph_2S_2 have been suggested. However, a type A coordination of the disulfide ligand occurs in $[CpFe(CO)_2(Ph_2S_2)](BF_4)$.²⁹

Similar complexes containing pyridine group, Py-S-S-Py, have also been reported. The complexes formulated as $[M(Py_2S_2)_2X_2]$, where M = Ni,

and X = CL, Br, CNS; M= Co, and X = Cl, Br, I; M = Hg, Zn and X = Cl; were structurally characterized.³⁰⁻³³ Interestingly Cu(I) and Cu(II) form the polymeric complexes $[\text{Cu}_2(\text{Py}_2\text{S}_2)_2\text{Cl}_2]$,³⁴ $[\text{Cu}(\text{Py}_2\text{S}_2)](\text{ClO}_4)$,³⁵ $[\text{Cu}(\text{Py}_2\text{S}_2)\text{Br}]_n$ and $[\text{Cu}(\text{Py}_2\text{S}_2)\text{Br}]_n$.³⁶ The Co(II) ion forms tetrahedral complexes, while the Ni(II) ion forms tetrahedral, square planar and five coordinate complexes, and the Zn(II) ion probably forms polymeric complexes. It was observed that the sulfur atoms are not involved in the coordination. The hard and soft acid character of each metal ion is probably a determinant factor in its coordination pattern. From this point of view, it is possible to understand why the Co(II) ion prefers to be coordinated by the two nitrogen atoms of Py_2S_2 ³¹ instead of one nitrogen atom and one disulphide sulfur atom, or why two Py_2S_2 molecules coordinate to the Cu(I) ion using two different donor sets, i.e. NS and NN .³⁵ $[\text{Cu}(\text{Py}_2\text{S}_2)_2]\text{ClO}_4$ is the only known complex in which the Py_2S_2 ligand binds to a metal ion through a disulfide sulfur atom. In some circumstances, then, an organic disulfide group can compete successfully with a pyridyl nitrogen atom for a transition metal ion coordination site.

Considering the structural diversity exhibited by disulfide complexes, we assume that the $(\text{BrPh})_2\text{S}_2$ ligand having two potential donor sulfur atoms would provide only one donor atom to any one metal center. It is feasible that the metal ions in the $[\text{ML}_2\text{Cl}_2(\text{H}_2\text{O})_2]$ (where M = Mn(II), Fe(II), Co(II) or Ni(II)) and $[\text{CrL}_2\text{Cl}_2(\text{H}_2\text{O})_2]\text{Cl}$ complexes are hexa coordinate with two molecules of $(\text{BrPh})_2\text{S}_2$ in trans positions, two chloride anions and two water molecules at the vertices of an octahedron. The presence of tetrahedral or polymeric structures with different dimensions cannot be discarded. Despite the crystalline nature of the products we could not succeed in obtaining single crystals, even after inordinate attempts, suitable for X-ray structure determination.

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