THE PREPARATION OF THE NEW COMPARTMENTAL LIGAND 1-(2-HYDROXYPHENYL)-3-(2-THIOMETHOXYPHENYL)-1,3-PROPANEDIONE AND ITS INTERACTIONS WITH METAL IONS

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Abstract—The preparation of the ligand 1-(2-hydroxyphenyl)-3-(2-thiomethoxyphenyl)-1,3propanedione (H₂htmp) is reported along with its physicochemical characterization. The compound is present in the solid state as an unique enol tautomer, while in solution both the enol and the keto tautomers are present. By reaction with metal salts, mononuclear complexes of the type $M(H_2htmp)_2Cl_2$ (M = Pt, Pd) and $M(Hhtmp)_2 \cdot 2H_2O$ (M = Cu, Ni and Co) were isolated and characterized by physicochemical measurements. In addition homo- and heterobinuclear complexes have been prepared.

The design and synthesis of coordination compounds containing two or more different metal ions in adjacent sites are interesting because they provide the path to study multi-electron redox reactions, magnetic exchange interactions and the possible activation of small substrate molecules. Moreover, these complexes can be used to mimic enzymatic metal sites.¹⁻⁴

To obtain heterobinuclear complexes we have prepared and studied the trinucleating ligand 1-(2-hydroxyphenyl)-3-(2-thiomethoxyphenyl)-1,3propanedione (H₂htmp) which presents three types of reacting sites, one in the centre of the molecule (the β -diketone moiety) and two in the outer sites (the β -ketophenyl and the thioether moiety).

This ligand gives mononuclear and homo- and heterobinuclear complexes allowing, consequently, the synthesis of MM'M'' linear trinuclear compounds that are otherwise difficult to obtain.⁵⁻⁷

The present paper reports the preparation of several mono- and binuclear complexes with this ligand. All the compounds described herein are airstable, both in the solid state and in solution.

EXPERIMENTAL

All the solvents used in the preparation were freshly distilled. Melting points were recorded on a

Fisher stage melting point apparatus and are not corrected. IR spectra were recorded on a Nicolet FTIR 5DX spectrometer as KBr pellets or in Nujol mulls. The electronic spectra were recorded on a Cary 17 UV spectrophotometer in DMSO solution and Nujol dispersion. The ¹H NMR spectra (200 MHz) were obtained on a Brucker spectrometer in CDCl₃ solution.

Preparation of 1-(2-hydroxyphenyl)-3-(2-thiomethoxyphenyl)-1,3-propanedione (H₂htmp)

o-Hydroxyacetophenone (50 mmol) was dissolved in toluene (15 cm³); two drops of methanol were added and the solution was slowly added to a 60% NaH suspension in toluene (170 cm³). The resulting yellow suspension was gently refluxed for 15 min. After which, a toluene solution (100 cm³) of methyl o-methylthiosalicylate (55 mmol) was added dropwise. The suspension was refluxed for 6 h, and then allowed to cool down to room temperature. The precipitate was filtered, washed with diethyl ether and dried in vacuo. It was added to icecooled water, stirred for 10 min, and then acidified to pH = 1 with conc. HCl and the solid extracted with diethyl ether. The organic phase was separated, washed with a 5% NaHCO₃ solution and water. After decantation of the aqueous phase, the ethereal phase was dried over Na_2SO_4 . Evaporation of the organic solution gave a yellow solid, which upon

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recrystallization from methanol gave 7.4 g of pure ligand, m.p. $69-70^{\circ}$ C (yield, 52%).

Preparation of $M(H_2htmp)Cl_2$ (M = Pd, Pt)

The ligand (2 mmol) was dissolved in benzene (100 cm^3) and the appropriate metal chloride (1 mmol) was added with stirring. The resulting solution was stirred for 48 h. The product was filtered, washed with benzene, ethanol and diethyl ether, and dried *in vacuo*. The same products were obtained when ethanol was used as solvent.

Preparation of $M(Htmp)_2 \cdot nH_2O(M = Cu, n = 0; M = Ni \text{ or } Co, n = 2)$

The ligand (2 mmol) was dissolved in ethanol and the appropriate metal acetate or chloride hydrate (1 mmol) was added with stirring. The resulting solution was stirred for 6 h. The obtained precipitate was filtered, washed with ethanol and diethyl ether, and dried *in vacuo*. The same products were obtained when benzene was used as solvent.

Preparation of homobinuclear $M_2(htmp)_2 \cdot H_2O$ complexes (M = Ni or Co, n = 4; M = Cu, n = 0)

An ethanolic solution of the ligand (2 mmol) and of lithium hydroxide (4 mmol) was added to a warm ethanol solution of the appropriate metal acetate (1 mmol). The resulting mixture was allowed to reflux for 8 h and then cooled to room temperature. The precipitate was filtered and washed several times with ethanol and diethyl ether, and then dried *in vacuo*.

Preparation of CuNi(htmp)₂·2H₂O

Lithium hydroxide (2 mmol) was added to an ethanolic suspension of the mononuclear com-

pound (1 mmol) and the solution was stirred at room temperature for 30 min. Then a solution of the metal acetate (1 mmol) in ethanol was added and the mixture refluxed for 8 h. The solid was filtered, washed with ethanol and diethyl ether, and dried *in vacuo*.

Preparation of PdCu(Hhtmp)₂Cl₂

The complex can be prepared by reaction of the mononuclear $Cu(Hhtmp)_2$ and $PdCl_2$, or of $Pd(H_2htmp)_2Cl_2$ and copper(II) acetate in an ethanolic solution.

RESULTS AND DISCUSSION

The ligand has been synthesized in three steps (see Scheme 1) starting from thiosalycylic acid. In the first step the thiolo group is methylated by methyl iodide. After conversion into the methyl ester it reacted with *o*-hydroxyacetophenone in the presence of sodium hydride.

The compound gives microanalytical and mass spectral data consistent with the structure; the fragmentation pattern of the compound is reported in Fig. 1. The X-ray structure of the ligand⁸ showed that the compound is present, at least in the solid state, only as its enol tautomer (see Fig. 2).

The hydroxyl IR stretching band of the ligand consists of a broad signal (400 cm⁻¹ wide) centred at approx. 3050 cm^{-1} ; this band may result from two broad, overlapping OH absorptions. Both the position and the extreme width are compatible with strong intramolecular association. In the carbonyl region only one band at 1609 cm⁻¹ is present, due to chelating C=O-H, while no band due to free C=O is observed.

The enol tautomer is the major form in CDCl₃ solution. A freshly prepared chloroform solution showed the presence of the enol form, together with







Fig. 1. Fragmentation pattern of 1-(2-hydroxyphenyl)-3-(2-thiomethoxyphenyl)-1,3-propanedione.

extraneous material, amounting to about 18%. The pre-eminent ¹H NMR resonances occur at 2.5, 6.75, 12 and 15.45 ppm and have been assigned to the CH_3S , CH, phenolic OH and enolic OH of the enol form, respectively. Other weak signals are at 2.4, 4.65 and 11.9 ppm and may be assigned to the SCH_3 , methylene and phenolic OH of the ketonic tautomer. The integration peak areas are in agreement with these assignments. The other multiple bands in the range 6.9–8.0 ppm are due to aromatic hydrogens.

Interaction with metal salts

Reactions of $PdCl_2$ or $PtCl_2$ with the ligand, in benzene or ethanol solution, gave compounds of



Fig. 2. Molecular structure of $C_{16}H_{14}O_{3}S$ and the atom labelling scheme.

the type $M(H_2htmp)_2Cl_2$. Both the cream-coloured platinum(II) and palladium(II) complexes present similar IR spectra; in the 1700–1400 cm⁻¹ region there are peaks at 1609, 1578 and 1562 cm⁻¹, present also in the free ligand, which are attributed to the C=O, benzene ring and C=C stretching modes, respectively. The complexes display a band at 385– 375 cm⁻¹ assigned to the v(M=S) stretching vibration, since this band is not present in the spectra of the free ligand or of other metal complexes. The two bands at 318 and 301 cm⁻¹, and 328 and 310 cm⁻¹, are assigned to the Pd—Cl and Pt—Cl stretches, respectively. We suggest a coordination geometry of the type shown in Fig. 3(A) for these complexes.

The ¹H NMR spectrum of $Pd(H_2htmp)_2Cl_2$, in d_6 -DMSO solution, is virtually identical to that of the free ligand; it shows that the organic moiety is uncoordinated to the palladium, at least in DMSO solution, and involved in a keto-enol equilibrium, where the enol tautomer is predominant. The preeminent peaks occur at 2.47 (SCH₃), 7.13 (CH), 11.6 (phenolic OH) and 15.75 (enolic OH). The 2.40 (SCH₃), 4.82 (CH₂) and 11.2 (phenolic OH) peaks can be assigned to the keto form. The integrated peak areas are in agreement with these assignments. From this solution a crystalline compound was obtained, and its elemental analysis agrees with the formula Pd(DMSO)₂Cl₂.

Compound	C (%)		H (%)		S (%)		Metal (%)	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
H ₂ htmp	67.1	67.6	4.9	4.9	11.2	11.3		
Cu(Hhtmp) ₂	60.6	60.7	4.1	4.2	10.1	9.8	14.2	14.0
$Ni(Hhtmp)_2 \cdot 2H_2O$	57.7	57.5	3.9	4.1	9.6	9.8	8.8	8.3
$Co(Hhtmp)_{2} \cdot 2H_{2}O$	57.7	57.6	3.9	4.0	9.6	9.8	8.8	8.5
$Pt(H_{2}htmp)_{2}Cl_{2}^{a}$	41.2	41.5	3.0	2.9	6.9	7.1	20.3	20.4
$Pd(H_{2}htmp)_{2}Cl_{2}^{b}$	51.2	51.6	3.8	3.7	8.5	8.3	14.2	13.8
$Cu_2(htmp)_2$	55.2	55.8	3.5	3.2	9.2	9.0	18.3	18.7
$Ni_{2}(htmp)_{2} \cdot 4H_{2}O$	50.7	50.3	3.7	3.3	8.4	8.1	15.5	15.8
$Co_2(htmp)_2 \cdot 4H_2O$	50.7	50.3	3.7	3.4	8.4	8.2	15.5	15.9
$CuNi(htmp)_{3} \cdot 2H_{3}O$	52.9	52.6	3.9	3.4	8.8	8.5	8.7(Cu)	8.3
							8.1(Ni)	7.8
$PdCu(Hhtmp)_2Cl_2^c$	47.4	47.7	3.2	3.0	7.9	7.6	7.8(Cu)	8.0
							13.2(Pd)	12.8

Table 1. Analytical data

^a Calc.: Cl, 7.6. Found: Cl, 8.0.

^b Calc. : Cl, 9.4. Found : Cl, 9.7.

^c Calc. : Cl, 8.7. Found : Cl, 8.9.

By reacting the ligand H₂htmp with copper(II), nickel(II) and cobalt(II) metal salts, in benzene or ethanol solution, complexes of the type $M(Hhtmp)_2 \cdot nH_2O$ have been obtained. Their almost identical IR spectra suggest that the same type of coordination is present in all the compounds. Characteristic absorption bands are found in the 1600–1500 cm⁻¹ region; on the basis of literature data,⁹ we assign the band occurring near 1610 cm⁻¹ in both the spectra to the C==O and the band at about 1510 cm⁻¹ to the C==C stretching modes of the coordinated acetylacetonate moiety. The absorption band at 3400 cm⁻¹ in the complexes containing water molecules is consistent with the analytical data. From these IR data either of the structures shown in Fig. 3(B) or (C) can be proposed for the 1:2 chelate.

The room temperature magnetic moments are in the range typical for planar copper(II) and octahedral nickel(II) and cobalt(II) complexes.

The electronic spectrum of the copper(II) shows a band at 670 nm, as expected for a square-planar copper(II) β -diketonate complex. Moreover, this band, which is attributed to the ligand field d-dtransition, is more similar to that of bis(dibenzoylacetonato)copper(II) than to that of bis(ohydroxyacetophenonato)copper(II) which has two peaks in this region. The nickel complex shows absorption bands between 500 and 1300 nm as expected for octahedral ones. The cobalt(II) com-



Fig. 3. (A) Proposed structure for $M(H_2htmp)_2Cl_2$, M = Pd or Pt; (B) and (C) possible structures of $M(Hhtmp)_2 \cdot nH_2O$, M = Cu, Ni or Co.

Compound	IR (cm^{-1}) frequency in the 1650–1500 cm ⁻¹ range			Ŭ	JV (nm)	μ (BM)	
H ₂ htmp	1610	1580	1560				
$Cu(Hhtmp)_2$	1614	1586	1538	670			1.78
$Ni(Hhtmp)_2 \cdot 2H_2O$	1612	1580	1527	680	1110		2.92
$Co(Hhtmp)_2 \cdot 2H_2O$	1600	1571	1516	530	600	1150	4.60
$Pd(H_2htmp)_2Cl_2$	1609	1578	1562				Diamagnetic
$Pt(H_2htmp)_2Cl_2$	1608	1580	1562		_		Diamagnetic
$Cu_2(htmp)_2$	1615	1590	1560	670 broa	ad		1.39
$Ni_2(htmp)_2 \cdot 4H_2O$	1610	1535	1510	650	1115		3.80
$Co_2(htmp)_2 \cdot 4H_2O$	1590	1543	1510	600			6.38
$CuNi(htmp)_2 \cdot 2H_2O$	1612	1585	1500	690	1100		2.59
PdCu(Hhtmp) ₂ Cl ₂	1615	1593	1560	670	—		1.82

Table 2. Spectroscopic data and magnetic moments

plex has a low intensity band at ca 1150 and two bands at 600 and 530 nm; these features are typical of a weak octahedral field, and the magnetic moment (4.60 BM) is of the same order as those found in other high-spin octahedral cobalt(II) complexes. We suggest that nickel, cobalt and copper are coordinated to the acetylacetone group as shown in Fig. 3(B).

Homobinuclear complexes

These complexes can be obtained by reaction of the ligand with the appropriate metal salts, or by reaction of the mononuclear compound with metal acetate. Their electronic and IR spectra suggest that these complexes are of the type shown in Fig. 4. The IR spectra show bands in the region 1650–1500 cm⁻¹, which are typical of coordinated carbonyl groups and ethylenic C=C bonds. The presence of water is confirmed by a broad band at 3450–3000 cm⁻¹, due to the stretching mode of coordinated



 $M = Cu^{2+}; Ni^{2+}; Co^{2+}$

Fig. 4. Probable structure for the linear homobinuclear complexes.

water. The electronic spectrum of the copper chelate in DMSO solution or in a Nujol mull, shows a broad band at 670 nm due to the d-d transition, as expected for copper(II) acetylacetonate or hydroxyacetophenonate complexes. The nickel(II) compound has very broad bands at 1100 cm⁻¹ and at 645 nm, similar to those found for some nickel(II) diketonate complexes.¹⁰ The electronic spectrum of the cobalt complex is very similar to that of Co(acac)₂ · 2py¹¹ and is consistent with octahedral coordination. The magnetic moments, at room temperature, of the dinuclear compounds are lower than the spin-only values, similar to those obtained for analogous adducts in which antiferromagnetic coupling is operative.¹²

Heterobinuclear complexes

The complexes can be prepared by reaction of the mononuclear complexes with the appropriate metal salts; however, it is necessary to pay attention to the temperature reaction since the copper and nickel mononuclear complexes can be converted into the 2/2 chelate by heating above 60° C. Their IR data are essentially the same as that of the corresponding homobinuclear complexes. The strong band in the 1585–1630 cm^{-1} region is attributable to the coordinated C=O group, and the band in the 1500–1570 cm⁻¹ region corresponds to the C=C vibration. Moreover, the PdCu(Hhtmp)₂Cl₂ complex shows bands due to the Pd-S and Pd-Cl stretching modes. The magnetic property is explained by assuming that the entire paramagnetism arises from the copper(II) centre; on this basis the magnetic moment is as expected for the isolated d^9 copper(II) ion.

The room temperature magnetic moment of NiCu(htmp)₂·2H₂O (2.59 BM) is lower than the

spin-only values, and is similar to those found for analogous complexes in which a magnetic exchange coupling takes place.¹³ Work is in progress to prepare the trinuclear chelates.

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