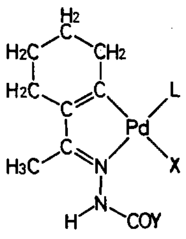
Similarly ν(Pd–Cl) (Table 3) are replaced by the bands at 268 and 200 cm^{-1} for $[PdBr(La)(PPh_3)]$ and at 246 cm^{-1} for $[PdBr(Lb)(PPh_3)]$. Presumably ν(Pd–X) (X = Cl or Br) are coupled with other modes of vibration. The low frequencies of these bands are, however, consistent with the structure where Cl or Br is coordinated *trans* to a carbon donor with a high *trans*-influence(7) (structure *5*).



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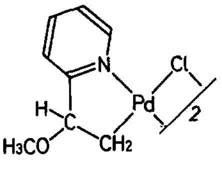
In the ^1H n.m.r. spectra of the free ligands the signals of the CH_2 groups appear as two separate multiplets with an intensity of 4 H (Table 2). The olefinic proton signal at *ca.* 6.3 ppm turns into a singlet upon irradiation of the lower field multiplet suggesting that it includes the signals of the CH_2 group adjacent to the double bond. Upon complexation to form $[PdClL]_2$ the lower field multiplet splits into two with an intensity of 2 H (Table 3). One of the two is down field and may be due to the CH_2 adjacent to the palladated carbon atom, for a considerable down field shift has been observed for the *ortho*-hydrogen of other cyclopalladated complexes(9).

In the spectra of the py and PPh_3 derivatives the chemical shifts of the CH_2 groups are markedly different from those of the parent and of the acac complex which show the signal of one CH_2 group at *ca.* 2.6 ppm. All the CH_2 signals of the py and PPh_3 complexes are at a higher field than 2.22 ppm (Table 3). Shielding can be induced by the magnetic anisotropies of the pyridine and phenyl rings of the ligands. In structure *5* one of the CH_2 groups adjacent to the double band may be in the shielding region of the aromatic rings.

The hydrazone derivatives of 1-acetylcyclohexene are easily cyclopalladated (structure *4*) with retention of the double bond. Cyclopalladation reactions of olefin derivatives such as 2-vinylpyridine and *N,N*-dimethylallylamine reported so far(4) usually result in addition of a Pd–X (X is a group such as OCH_3) group across the double bonds to form the complexes such as $[\overline{PdCl(CH_2CH(OCH_3)C_5H_4N})]_2$ and $[\overline{PdCl(CH_2CH(OCH_3)CH_2N}(CH_3)_2]_2$ and do not result in replacement of a hydrogen atom (structure *6*). In the present case the olefin bond is a member of a cyclohexene ring and the conformation is rigid. This favours replacement rather than addition which supports the proposition suggested previously(5).



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Synthesis and Characterization of Barbituric and Thiobarbituric Acid Complexes

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Summary

Synthesis of barbituric and thiobarbituric acid complexes derived from cobalt(II), nickel(II) and copper(II) salts were carried out. The elemental analyses suggest a range of stoichiometries, 1:1, 1:2 and 1:3. Electronic spectra and magnetic susceptibility measurements were used to infer the structures. The i.r. spectra of the ligands and their complexes are used to identify the type of bonding.

Introduction

Barbiturates are malonylurea derivatives with different substituents in the C-5 position(1–16). This paper describes the syn-

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thesis and characterization of Co^{II}, Ni^{II} and Cu^{II} complexes of barbituric (A) and thiobarbituric (B) acid.

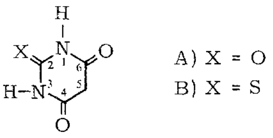


Figure 1. Structures and numbering of ligands.

Experimental

Barbituric and thiobarbituric acids were obtained as reagent grade materials and were used without further purification. The ligand (0.01 mole) in EtOH (25 cm^3) was mixed with the metal chloride (0.01 mole) in EtOH (25 cm^3) and in presence of concentrated ammonia (5 cm^3). The mixture was stirred for 30 minutes at 45 °C. The precipitate was filtered and washed several times with EtOH and dried *in vacuo* over $CaCl_2$. The analytical data are collected in Table 1.

Table 1. Colour, analysis and magnetic moments of barbituric acid (H_2L) and thiobarbituric acid (H_2L') complexes.

Complex	Colour	% Calc. (Found) S	N	Cl	M	μ(B.M.)
CoL_3Cl[a]	Violet	– –	17.6 (17.5)	7.4 (7.35)	12.7 (12.3)	dia.
NiL_3Cl[a]	Green	– –	17.6 (17.7)	7.4 (7.4)	12.3 (12.0)	2.3
$CuL\ H_2O$[b]	Blue	– –	12.5 (12.9)	– –	28.0 (27.9)	0.5
$CuL_2\ H_2O$[b]	Green	– –	16.7 (16.5)	– –	18.6 (18.7)	dia
$CoL'_2\ Cl\ H_2O$[a]	Pink	15.9 (15.8)	14.0 (14.3)		14.7 (14.9)	0.83
$NiL'_2\ Cl$[a]	Pale green	16.7 (16.6)	14.6 (14.5)		15.3 (15.3)	dia.
$CuL'_2\ H_2O$[b]	Brown	17.4 (17.3)	15.2 (15.2)	– –	17.3 (17.3)	dia.

[a] Soluble in H_2O. [b] Insoluble in H_2O.

The i.r. were recorded using a Pye Unicam SP 2000 spectrophotometer and KBr discs. The electronic spectra were measured using a Pye Unicam SP 1750 spectrophotometer. The room temperature Gouy measurements on powdered complexes were used for obtaining the magnetic moments. $Hg[Co(SCN)_4]$ was used for calibration and the diamagnetic corrections were made using Pascal's constants.

Results and Discussion

The reactions of metal ions with biologically active compounds have attracted great attention(17). The reaction of barbituric acid with transition metal salts yields beautiful powders which are quite stable in the atmosphere. Copper complexes of barbituric acid have 1 : 1 and 1 : 2 stoichiometries, but both cobalt and nickel have 1 : 3. All the thiobarbituric acid complexes are of the stoichiometry 1 : 2 (Table 1). The copper complexes contain no chloride but the cobalt and nickel complexes do. There are few examples of N,S-donor octahedral tris(chelate) complexes(18), particularly where the chelate ring would be four-membered, and hence highly strained. Where such chelates do occur, they are usually of the inner complex type(19).

Barbituric acid gives a violet complex CoL_3Cl while thiobarbituric acid gives a pink complex $CoL_2Cl \cdot H_2O$. There is little information on the electronic spectra of (N,S) or (S,S) low-spin, square-planar Co^{II} complexes(20). The magnetic moments of cobalt complexes derived from barbituric and thiobarbituric acids were found to be zero and 0.83 B.M., respectively. This anomaly may be due to one of the following. i) A ferromagnetic impurity in a low-spin complex. However, the magnetic moments of the complexes are independent of the field strength; which excludes this. ii) An antiferromagnetic interaction in a high-spin complex. iii) An admixture of a diamagnetic Co^{III} complex arising from air-oxidation with high-spin Co^{II} complexes. iv) Either a Boltzman distribution over different spin-states, or a mixing of $^2E(^2G)$ and $^4T_1(^4F)$ states, an equilibrium between high-spin and low-spin configurations. The electronic spectra of the cobalt complexes suggest an octahedral configuration. The thiobarbituric acid system absorbs at shorter wavelengths than the oxygen homologue. The spectral data are strongly blue-shifted in DMSO, implying a strong solute-solvent interaction.

Nickel(II) complexes may have u.v.-vis. spectra consisting of more than one band arising from the different d-d transitions in d^8 complexes. The strong band at 270 nm in the spectrum of NiL_3Cl is due to the inter-ligand electronic transitions. This band remains at the same position in presence of DMSO (Table 2). The broad band located at 520 nm is probably due to the $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) transition in a distorted octahedral configuration. The electronic spectrum of NiL'_2-Cl is red-shifted compared to that of the oxygen homologue. The diamagnetism and the lack of absorption at $\lambda > 800$ nm suggests a singlet ^1A_g ground state and consistent with a square-planar structure. The broad band at 670 nm could be a d-d transition of square-planar Ni^{II}, mainly $^1A_{1g} \rightarrow {}^1A_{2g}$ transition(21). The room temperature magnetic moment of NiL_3-Cl is 2.3 B.M. which is below the spin-only for two unpaired electrons. This suggests the existence of some quenching property, possibly Ni–Ni interaction or equilibrium between high-spin ($S = 1$) and low-spin ($S = 0$) configurations(22).

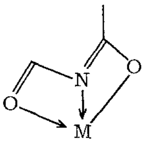
Copper(II) is a class B metal and would be expected to have a high affinity for sulphur. The 1 : 1 and 1 : 2 copper-barbituric acid complexes are blue and green while the 1 : 2 thiobarbituric acid complex is brown. The blue has $\mu_{eff} = 0.50$ B.M., while the green and brown complexes are diamagnetic. The low

Table 2. $\lambda_{max.}$ for the prepared complexes in the solid state and in presence of DMSO

Complex	$\lambda_{max.}$(nm) Nujol	DMSO
$CoL_3\ Cl$	250(m), 400(s) 450(m), 710(b)	270(s), 300(b) 440(b), 470(b)
$CoL'_2\ Cl \cdot H_2O$	290(b), 370(m), 550(s)	270(w), 290(s), 450(s)
$NiL_3\ Cl$	270(s), 520(b)	270(s), 460(m)
$NiL'_2\ Cl$	300(s), 670(b)	300(s), 550(m)
$CuL\ H_2O$	250(s), 290(b), 650(b)	272(s), 410(b)
$CuL_2\ H_2O$	250(s), 410(b), 660(b)	245(s), 375(m), 500(m)
$CuL'_2\ H_2O$	260(m), 290(s), 460(w)	260(w), 290(s), 450(vw)

effective magnetic moment of the blue complex is consistent with strong antiferromagnetic spin-spin interaction through molecular association(23). This is consistent with tetragonal distorted O_h geometry about Cu^{II} of approximate D_{4h} symmetry and can be ascribed to the $^2E_g \rightarrow {}^2B_{1g}$ transition. The diamagnetic property of the bis(complexes) can be attributed to strong Cu–Cu interaction or reduction of Cu^{II} to Cu^{I}.

The elemental analyses (Table 1) and i.r. spectra (Table 3) suggest that the mode of bonding in barbituric acid complexes is as follows



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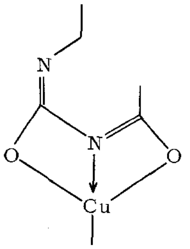


(2)

Table 3. Infrared spectra (cm^{-1}) of barbituric acid (H_2L) and its complexes

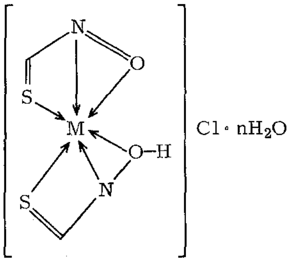
H_2L	CoL_3 Cl	NiL_3 Cl	CuL H_2O	CuL_2 H_2O	Assignment
3590(s)	3540(s)	–	–	–	ν$(OH)_{as}$
3490(s)	–	3400(sh)	3400(sh) 3300(m)	–	ν$(OH)_s$
3200(s)	3150(b)	3150(b)	3210(m)	3200(b)	ν(NH)
1730(b)	1640(b)	1650(b)	1600(m)	1650(b) 1605(m)	ν(C=O), ν(C=N)
1550(b)	1485(w)	1490(w)	–	1490(w)	Amide I
1410(w)	1405(w)	1400(s)	1400(w)	1415(w)	δ(NH)
1350(m)	1345(s)	1350(m)	1345(w)	1345(s)	ν(C=N)
1280(m)	1295(s)	1300(s)	1260(s)	1300(s)	ν(C–O), δ(O–H)
1195(m)	1210(m)	1215(s)	1235(m)	1215(w)	ν(C–N)
1070(w)	1085(w)	1090(w)	1115(s)	1115(w)	ν(C–O), ν(C–N)
855(m)	840(b)	860(m)	–	825(m)	ϱ(O–H)
660(s)	680(sp)	680(sp)	–	685(w)	δ(C=O)
–	530(s)	540(s)	–	540(s)	ν(M–N)
–	430(b)	430(m)	460(w)	440(b)	
–	215(s)	225(s)	210(s)	220(s)	ν(M–O)

Table 4. Infrared spectra (cm^{-1}) of thiobarbituric acid (H_2L') and its complexes

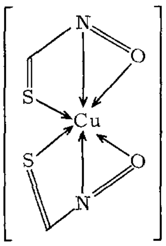
H_2L'	CoL'_2 Cl · H_2O	NiL'_2 Cl	CuL'_2 H_2O	Assignment
–	3110(b)	3120(b)	3100(b)	ν(N–H)
3000(b)	–	3000(b)	3000(b)	ν(O–H)
1720(m)	1720(s)	–	–	ν(C=O)
1650(m)	–	–	–	ν(C=O)
1615(w)	1620(b)	1620(b)	1620(b)	ν(C=O)
1570(m)	1550(sh)	1550(sh)	1560(sh)	δ(N–H) + ν(C=C); ν(C=O) + ν(C=N)
1400(w)	1400(vs)	1400(s)	1400(s)	δ(N–H)
1350(s)	–	–	–	ν(C=N) + ν(C=S)
1295(m)	1300(s)	1300(s)	1300(s)	δ(O–H)
1240(s)	1220(w)	1220(w)	1220(w)	ν(C=S) + ν(C–N)
1160(s)	1190(s)	1200(s)	1190(s)	ν(C–N) + ν(C=S)
990(w)	1115(s)	1000(sp)	1000(sp)	ν(C–O), ν(CS) + ν(CN)
930(s)	890(w)	900(m)	900(m)	δ(C–H)
820(s)	790(m)	795(s)	795(s)	
600(s)	620(s)	610(w)	610(w)	ν(M–N)
530(s)	535(s)	535(s)	540(s)	
225(s)	240(s)	250(s)	250(s)	ν(M–S)

Upon coordination of thiobarbituric acid, the following changes occur (Table 4): a) the disappearance of ν(C=O) at 1720 and 1650 cm^{-1} and the appearance of a new band at 1620 cm^{-1}, b) the strong band at 1530 cm^{-1} disappears. However, the complexes still possess characteristic bands for ν(NH), ν(OH), δ(NH) and δ(OH) (Table 4).

The coordination of thioketo-sulphur should cause an increase in the C–N bond order and lowering of frequency of ν(CS). The thione group takes part in complexation with no enthiolization process. All the evidence is consistent with this ligand behaving in a tridentate fashion. The structures of the thiobarbituric acid complexes can be formulated as follows



M = Co; n = 1
M = Ni; n = 0
(3)



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