tion of the complexes in methanol, probably yielding Cu(terpy)$^{2+}$ and phenolate at low concentrations. In DMSO, however, both the molar conductance and absorptivity remain nearly constant even at low concentration. For the five complexes containing *p*-methoxy, *p*-Cl, *p*-Br, *p*-F, *o*-NO_2 or *m*-NO_2-phenolate, no distinct phenolate absorption appears in the visible region, rendering it impractical to monitor the behaviour of these complexes at low concentration. However the molar conductivities display sharp increases at low concentrations ($<1 \times 10^{-4}$ M) in methanol, indicative of similar behaviour as for the nitrophenolates.

The solution and frozen-glass EPR spectra of these complexes in 5:1 methanol:water at low concentrations lend further support to the presence of non-bridging phenolate in these complexes as well as to the partial dissociation. Thus at 77 K the spectra are well-resolved, indicating that these complexes are monomeric (Table I). Furthermore the spin-Hamiltonian parameters [$g_{/\!/}$, $g_{\perp}$, $A_{/\!/}$ ($^{63/65}$Cu)] are typical of tetragonal Cu(II) complexes. Substantial covalency of the Cu-N bond is evidenced by the seven well-defined N-14--superhyperfine structure on the $g_{\perp}$ component, demonstrating the equivalence of the three pyridyl N. At ambient temperature, however the spectra are poorly resolved, displaying striking resemblance to that reported recently for [Cu(tery)]$^{2+}$ [6]. In the latter the poorly resolved spectrum has been attributed to dynamic Jahn-Teller effect.

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PS5.25 — TU

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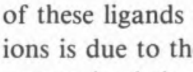
COMPLEX FORMATION IN THE SYSTEM Ni(II) — α-MERCAPTOPHENYLACETIC ACID

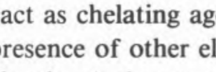
INTRODUCTION

The complex chemical significance of biologically active ligands like L-cysteine and D-penicillamine is determined by the mercaptosulphur donor atom, which is quite soft in character. The ability of these ligands to act as chelating agents of metal ions is due to the presence of other electron donor groups in their molecule. A deeper understanding of this type of chelate formation requires extension of research into studies of the effect of different substituents in the chelation properties of a ligand. The aim of the present work is to study the influence of the presence of a phenyl group in the Ni(II) complexing activity of aliphatic α-mercaptoacids.

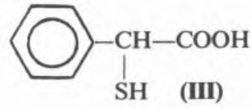
It has been reported that α-mercaptoacetic acid **(I)** forms polynuclear — Ni_3L_4, Ni_4L_6 — and mononuclear — NiL_2 — complexes [1-3]. The same species excluding the Ni_4L_6 have been considered for α-mercaptopropionic acid **(II)** [4]. In this study formation constants for the Ni(II) complexes of α-mercaptophenylacetic acid **(III)** have been determined.



$\mathrm{H{-}\underset{\substack{|\\ SH}}{CH}{-}COOH}$ **(I)**



$\mathrm{CH_3{-}\underset{\substack{|\\ SH}}{CH}{-}COOH}$ **(II)**



(III)

EXPERIMENTAL

The protonation constants of the ligand and the formation constants of the metal complexes have been determined at 25°C and 1 M ClO_4^- in 50% ethanol/water (v/v) using glass electrode potentiometry. The study has been carried out in an ethanol-water mixture because of the insolubility of the ligand in water.

The following cell, which includes a Wilhelm bridge [5], was used:

Ag,AgCl(s)	0.010 M NaCl 0.990 M $NaClO_4$ (50% eth./w.)	1 M $NaClO_4$ (50% eth./w.)	TS	Glass electrode

The electrode system was calibrated in terms of hydrogen ion concentration by performing strong acid *versus* strong base titrations [6].

In the determination of the protonation constants the hydrogen ion concentration was varied by addition of a T1 solution to a TS solution:

T1: $-H_1$ M H^+; 1 M ClO_4^-
(50% ethanol/water (v/v))

TS: A_o M H_2L; H_o M H^+; 1 M ClO_4^-
(50% ethanol/water(v/v))

In the study of the metal complexation, the total metal concentration was kept constant by adding equal volumes of T1 and T2 to a new TS solution:

T2: $2B_o$ M Ni^{2+}; H_2 M H^+; 1 M ClO_4^-
(50% ethanol/water (v/v))

TS: B_o M Ni^{2+}; A_o M H_2L; H_o M H^+; 1 M ClO_4^-
(50% ethanol/water (v/v))

Protonation curves for the ligand were obtained at a variety of different total ligand concentrations. Metal complex formation curves were obtained at different ligand:metal ratios and for different total ligand and metal concentrations. Experimental data was treated using the ESTA library [7] as described previously [8]. All calculations were performed on a VAX 11/780 computer (UWIST, Cardiff).

RESULTS AND DISCUSSION

Formation constants obtained in the present work are listed in Table 1. The finding of the Ni_3L_4, Ni_2L_3 and NiL_2 complexes confirms that ligands containing a mercapto group tend to form complexes where sulphur bridges link two or more metal ions. The lack of formation of the Ni_4L_6 complex, reported for α-mercaptoacetic acid, can be caused by steric hindrance due to the presence of a phenyl group in the molecule. It also may be noted that this presence gives the complexes greater stability.

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Table 1

	p	q	r	lg β_{pqr}	U	S.S.R.	Points	Titrations
H^+	0	1	1	10.366 ± 0.001	521.5	2.180 E-06	498	9
	0	1	2	14.420 ± 0.002				
Ni^{2+}	3	4	0	40.437 ± 0.013	131.7	3.894 E-06	615	15
	2	3	0	28.819 ± 0.008				
	1	2	0	16.717 ± 0.003				

PS5.26 — TH

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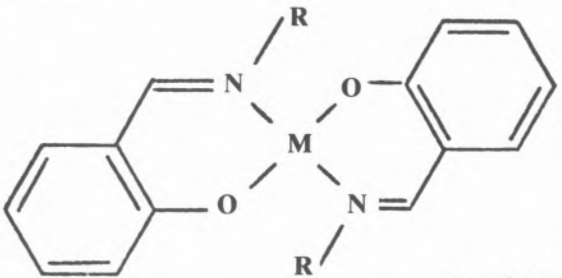
KINETICS OF LIGAND SUBSTITUTION IN CHELATE COMPLEXES OF DIVALENT TRANSITION METALS OF BIOLOGICAL IMPORTANCE

The bis chelate complexes M(sal-R)$_2$ of divalent transition metals M^{2+} (M = Co,Ni,Cu,Zn) with various *N*-alkyl salicylaldimines Hsal-R (R = Et,*n*-Pr,*i*-Pr,*t*-Bu,*neo*-Pe,Ph) have been prepared by standard procedures and characterized.



M(sal-R)$_2$

Stopped-flow spectrophotometry has been used to study the reactivity of these complexes towards ligand substitution with acetylacetone (Hacac) in methanol under pseudo first-order conditions ($[\mathrm{Hacac}]_0 \gg [\mathrm{M(sal\text{-}R)_2}]_0$) according to (1):

$$\mathrm{M(sal\text{-}R)_2 + 2\ Hacac \rightarrow M(acac)_2 + 2\ Hsal\text{-}R} \qquad (1)$$

The experimental rate law is a two-term rate law:

$$\mathrm{rate} = (k_S + k_{\mathrm{Hacac}}[\mathrm{Hacac}])[\mathrm{M(sal\text{-}R)_2}] \qquad (2)$$

The substitution of the first ligand in M(sal-R)$_2$ is rate determining, *i.e.*, the conversion M(sal-R)(acac) → M(acac)$_2$ is a fast consecutive step.

The relative contributions of the terms k_S and k_{Hacac}[Hacac] in (2) to the overall rate are mainly controlled by two factors, namely, (i) by the type of the *N*-alkyl group R for a given metal M, and, (ii) by the type of metal M for a given *N*-alkyl group R.

The data obtained for k_S and k_{Hacac} at 25°C for the 24 reactions studied are presented. The rate constants range from $k_S \approx 0$ (M = Ni; R = Et,*i*-Pr,*neo*-Pe) to $k_S = 18.5\ \mathrm{s^{-1}}$ (M = Zn; R = Ph) and from $k_{\mathrm{Hacac}} \approx 0$ (M = Cu,Zn; R = *t*-Bu) to $k_{\mathrm{Hacac}} = 2070\ \mathrm{M^{-1}\,s^{-1}}$ (M = Ni; R = Et). The trends observed for the reactivity of the various complexes are correlated with their coordination geometry (as controlled by the *N*-alkyl group R) and with the intimate mechanism of both the solvent-induced pathway k_S and the ligand-dependent pathway k_{Hacac}[Hacac].

PS5.27 — MO

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COORDINATING PROPERTIES OF PYRIDOXAL THIOSEMICARBAZONE IN METAL COMPLEXES

The study of transition metal complexes of thiosemicarbazones is of great interest because of their pharmacological properties [1-3]. As part of a continuing interest in the chelating behaviour of ligands which have biological activities and the