A Physico-chemical Study of the Copper(II) Chelates of 3-Hydroxyphenylrhodanine. Its Mixed-ligand Chelate Formation and Conversion into a Copper(II) Dithiocarbamate Chelate

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The highly coloured copper(II) chelates of 3-hydroxyphenylrhodanine [3-(3-hydroxyphenyl)-2-thioxo-1,3-thiazolidin-4-one] and (4,5-dibromo-3-hydroxyphenyl)rhodanine have been prepared and characterised by elemental analysis, i.r. spectroscopy, and magnetic susceptibility measurements. The 3-hydroxyphenylrhodanine chelate has been shown to be useful in the sensitive spectrophotometric determination of copper(II). E.s.r. measurements show that the chelate forms a tetrapyridine solvate in pyridine solution. Mixed-ligand chelates consisting of copper(II) and 3-hydroxyphenylrhodanine and an amino-acid such as threonine, or a polyaminocarboxylic acid such as ethylenediaminetetra-acetic acid, have also been prepared and characterised. Dissolution of these copper(II) chelates of rhodanine in chloroform leads to the formation of the dithiocarbamate chelates bis(*N*-chloroacetyl-*N*-3-hydroxyphenyldithiocarbamato)copper(II) and bis(*N*-chloroacetyl-*N*-4,5-dibromo-3-hydroxyphenyldithiocarbamato)copper(II).

VARIOUS derivatives of rhodanine (2-thioxo-1,3-thiazolidin-4-one) have been described for the sensitive colorimetric determination of copper(II),[1] while the use of 3-hydroxyrhodanine in the colorimetric determination of copper(II) has been mentioned.[2] The present study is concerned with the isolation and chemical properties of the copper(II) chelates of 3-hydroxyphenylrhodanine.

RESULTS

Preparation and Properties of the Chelates of 3-*Hydroxyphenylrhodanine with* Cu^{II}, Zn^{II}, *and* Ni^{II}.—The copper(II) chelates of the ligands *N*-3-hydroxyphenylrhodanine [3-(3-hydroxyphenyl)-2-thioxo-1,3-thiazolidin-4-one] and (4,5-dibromo-3-hydroxyphenyl)rhodanine, the ligand anions of which may be designated as $(L^1)^-$ and $(L^2)^-$ respectively, may be prepared by addition of an acetone solution containing the ligand and 2 mol equivalents of triethylamine to an aqueous solution of copper(II) nitrate. In each case the copper(II) chelate precipitates from solution as a dark red-brown solid. As outlined by the analytical data in Table 1, the compositions of the chelates may be represented as $Cu(L^1)_2 \cdot 2H_2O$ and $Cu(L^2)_2 \cdot 2H_2O$. If the base, triethylamine, is omitted the copper(II) chelate isolated has the composition $Cu(HL^1)_2(NO_3)_2$. The chelates are soluble in a number of organic solvents and may be recrystallised from acetone or pyridine (py), whereby the copper(II) chelate of *N*-3-hydroxyphenylrhodanine is obtained in the forms $Cu(L^1)_2 \cdot 2Me_2CO$ or $Cu(L^1)_2 \cdot 4py$.

Magnetic susceptibility measurements on the chelates $Cu(L^1)_2 \cdot 2H_2O$ and $Cu(HL^1)_2(NO_3)_2$ gave values of $\mu_{eff.}$ 1.97 and 1.82 B.M.† respectively.

The C=O stretch band (1 709 cm^{-1}), thioamide band (III) (1 083 cm^{-1}), and thioamide band (IV) (786 cm^{-1}) in the i.r. spectrum due to rhodanine are observable for the ligand 3-hydroxyrhodanine and the dibromo-derivative. In each case the C=O band is a prominent feature of the spectrum. In the i.r. spectra of the rhodanine ligands most of the other bands can be assigned to the 3-hydroxyphenyl radical and these include bands due to aromatic ring vibrations in the 750—900 cm^{-1} region. The i.r. spectrum recorded on Nujol mulls of the zinc(II) chelates of 3-hydroxyphenylrhodanine shows that the C=O stretch at 1 710 cm^{-1} is still as prominent as in the free ligand and that its relative intensity compared with other components of the spectrum, such as bands due to aromatic ring vibrations, is unchanged. The thioamide bands (III) and (IV) cannot be observed. In the i.r. spectrum of the nickel(II) chelate of 3-hydroxyphenylrhodanine the C=O stretch band is clearly observed. Unfortunately the copper(II) chelate of 3-hydroxyphenylrhodanine gives a poorly resolved i.r. spectrum when recorded from a Nujol mull, however when recorded in acetonitrile solutions good quality spectra are obtained which show a prominent C=O stretch band at 1 720 cm^{-1}. Finally, the i.r. spectrum of the copper(II) chelate, recorded as a Nujol mull and prepared in the absence of base, namely $Cu(HL^1)(NO_3)_2$, shows a prominent C=O stretch band.

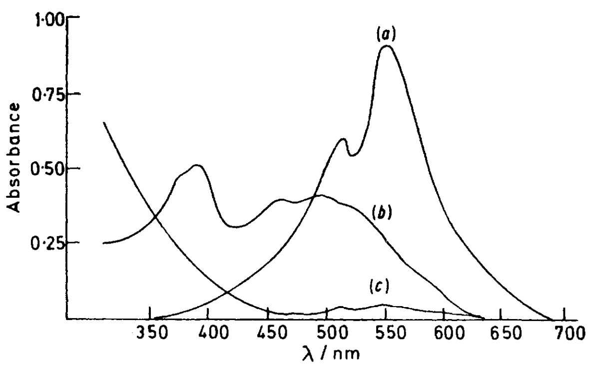

FIGURE 1 U.v.–visible absorption spectra using 1-cm pathlength glass cells of dmf solutions containing (*a*) $Cu(L^1)_2$, 5.0×10^{-5} mol dm^{-3}, (*b*) $Cu(HL^1)(NO_3)_2$, 5.0×10^{-5} mol dm^{-3}, (*c*) the ligand HL^1, 5.0×10^{-5} mol dm^{-3}

The unchanged intensity of the C=O stretch band in the copper(I) complexes of rhodanine has been taken to indicate the absence of co-ordination by the carbonyl group of rhodanine.[3] A similar conclusion is possible for the chelates of copper(II), zinc(II), and nickel(II) studied here.

The copper(II) chelate of 3-hydroxyphenylrhodanine dissolves in a number of organic solvents to give highly coloured solutions as indicated by Figure 1, which shows the electronic spectra in the visible region for $Cu(L^1)_2$ and Cu-

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† Throughout this paper: 1 B.M. ≈ 9.27×10^{-24} A m^2.

$(HL^1)_2(NO_3)_2$ in dimethylformamide (dmf) solution. The intensity of the band in the 550 nm region is diminished to some extent in pyridine and acetone solutions such that the optical density of 0.923 observed in dmf solutions 5.0×10^{-5} mol dm^{-3} with respect to $Cu^{II}(L^1)_2{\cdot}2H_2O$ falls to 0.869 in pyridine and 0.823 in acetone. Although the chelate $Cu(L^1)_2{\cdot}2H_2O$ is sparingly soluble in water, an aqueous solution containing 10% v/v of acetone can be formed by addition of an acetone solution of the ligand (5.0×10^{-4} mol dm^{-3}) to an aqueous solution of copper(II) nitrate (5.0×10^{-5} mol dm^{-3}) followed by the addition of one or two drops of concentrated aqueous ammonia. The optical density of the solution monitored at 550 nm is linearly dependent on the initial copper(II) concentration and provides a basis for the sensitive spectrophotometric determination of copper(II).

TABLE 1

Analytical data for the chelates. Calculated values are in parentheses

Compound [a]	Analysis (%) C	H	N	S
(*a*) 3-Hydroxyphenylrhodanine chelates				
$Cu(L^1)_2{\cdot}2H_2O$	43.2	3.10	5.65	24.2
	(43.35)	(2.95)	(5.40)	(23.7)
$Cu(L^2)_2{\cdot}2H_2O$	24.8	1.30	3.35	14.65
	(24.9)	(1.40)	(3.30)	(14.75)
$Zn(L^1)_2{\cdot}2H_2O$	39.1	2.95	5.30	22.9
	(39.15)	(2.90)	(5.15)	(23.15)
$Ni(L^1)_2{\cdot}2H_2O$	39.2	2.70	5.20	22.8
	(39.65)	(2.95)	(5.15)	(23.5)
$Cu(L^1)_2{\cdot}2Me_2CO$	44.7	3.10	4.65	22.1
	(44.5)	(3.20)	(4.60)	(21.75)
$Cu(L^1)_2{\cdot}4py$	55.2	3.75	10.2	15.25
	(55.15)	(3.80)	(10.15)	(15.3)
$Cu(HL^1)_2(NO_3)_2$	35.9	2.85	9.25	20.05
	(35.6)	(2.95)	(9.20)	(20.4)
(*b*) Mixed-ligand chelates				
$Cu(ThrO)(Thr)_{0.5}\text{-}L^2$	28.75	2.75	6.80	10.7
	(28.95)	(2.85)	(6.85)	(10.65)
$Cu(ThrO)L^1$	38.0	3.50	6.70	15.65
	(38.2)	(3.50)	(6.85)	(15.15)
$Cu(H_2edta)(HL^2)$	29.05	2.30	5.90	9.20
	(30.15)	(2.40)	(5.80)	(8.85)
$Cu(H_2edta)(HL^1)$	40.2	3.35	7.50	11.7
	(39.95)	(3.45)	(7.60)	(11.65)
$Ni(ThrO)L^2$	27.0	2.35	5.10	11.75
	(27.4)	(2.25)	(5.10)	(11.65)
$Ni(ThrO)L^1$	38.0	3.20	6.65	15.0
	(38.1)	(3.20)	(6.65)	(15.15)
(*c*) Dithiocarbamates				
$Cu(L^3)_2$ [b]	39.75	2.55	5.05	23.2
	(39.4)	(2.50)	(5.05)	(23.15)
$Cu(L^4)_2$ [c]	23.8	1.15	3.05	14.15
	(23.8)	(1.15)	(6.10)	(14.15)
$Cu(L^5)_2$	38.7	2.75	6.32	29.4
	(38.95)	(2.80)	(6.50)	(29.65)

[a] $HL^1 = SC(S)N(C_6H_4OH\text{-}3)C(O)CH_2$, $HL^2 = SC(S)N[C_6H_2(Br_2\text{-}4,5)(OH\text{-}3)]C(O)CH_2$, $L^3 = {}^-S_2CN(COCH_2Cl)(C_6H_4OH\text{-}3)$, $L^4 = {}^-S_2CN(COCH_2Cl)[C_6H_2(Br_2\text{-}4,5)(OH\text{-}3)]$, $L^5 = {}^-S_2CNH(C_6H_4OH\text{-}3)$. [b] Chlorine analysis 12.3% (12.45). [c] Chlorine analysis 6.90% (6.95).

The e.s.r. spectrum recorded at 77 K on an acetone solution containing the chelate $Cu(L^1)_2{\cdot}2Me_2CO$ (5.0×10^{-3} mol dm^{-3}) is shown in Figure 2. The e.s.r. spectrum of a pyridine solution of the chelate $Cu(L^1)_2{\cdot}4py$ is illustrated in Figure 3, where at higher instrumental gain extra-hyperfine interactions are observed appropriate to the interaction of the unpaired electron of the copper(II) ion with four ^{14}N nuclei in the tetrapyridine form of the chelate.

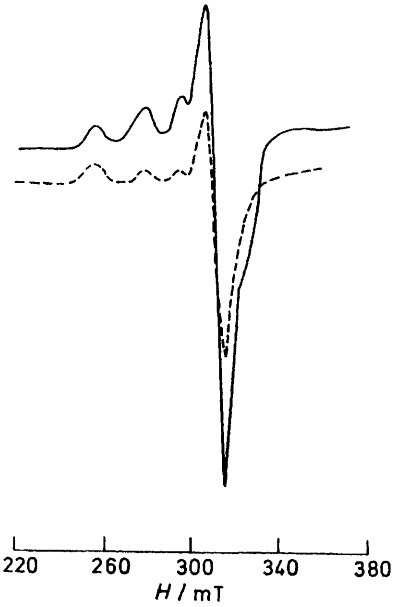

FIGURE 2 E.s.r. spectrum of an acetone solution of $Cu(L^1)_2{\cdot}2Me_2CO$ (5.0×10^{-3} mol dm^{-3}) at 77 K. The dashed curve shows the computer simulation using the parameters listed in Table 2

The magnetic parameters associated with the e.s.r. spectra depicted by Figures 2 and 3 were determined by computer simulation of the experimental spectra using an

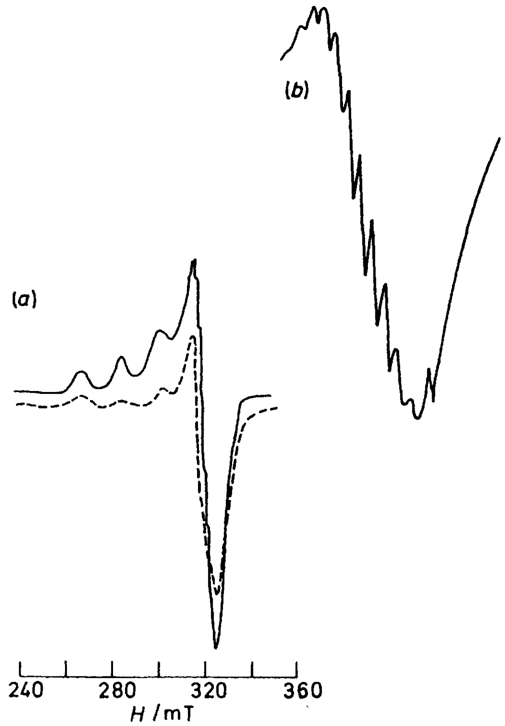

FIGURE 3 E.s.r. spectrum of a pyridine solution containing (*a*) $Cu(L^1)_2{\cdot}4py$ (5.0×10^{-3} mol dm^{-3}) at 77 K, (*b*) the $g_\perp$ region of the spectrum recorded at higher gain. Dashed curve as in Figure 2

axially symmetric spin Hamiltonian of the form (1), where the terms have their usual meaning and $S = \frac{1}{2}$, $I = \frac{3}{2}$,

$$\mathscr{H} = g_{\parallel}H_zS_z + g_{\perp}(H_xS_x + H_yS_y) + A_{\parallel}S_zI_z = A_{\perp}(S_xI_x + S_yI_y) \quad (1)$$

and $A_{\parallel}$ and $A_{\perp}$ are the copper(II) hyperfine constants. The magnetic parameters determined by computer simulation of the experimental spectra are summarised by Table 2.

Formation of Mixed-ligand Chelates.—In experiments designed to indicate the strength of ligation of the 3-hydroxyrhodanine to copper(II) by studying the ease of formation of the chelate under conditions of competitive chelation such as those provided by the addition of a solution of the rhodanine ligand to an aqueous solution containing copper(II) in the form of its ethylenediaminetetra-acetate (edta) chelates or threonine chelates, it was observed that instead of the expected replacement reaction to form the 3-hydroxyphenylrhodanine chelates or persistance of the copper(II) in the form of its edta or threonine derivative, a dark brown crystalline product separated from solution. Comparison of the solubility properties of this product with that of the copper(II) 3-hydroxyphenylrhodanine chelate established immediately that some other chelate form of copper(II) is produced in these circumstances. The analytical results of the isolated product as outlined by Table 1 indicate the formation of mixed-ligand chelates produced by the retention of the edta or threonine by the copper(II) ion and the acquisition of 3-hydroxyphenylrhodanine. Additional evidence for the formation of a mixed-ligand chelate rather than some other ligand produced by a condensation reaction of the components stems from the recovery of edta or threonine after treatment of the mixed-ligand copper(II) chelate with dilute hydrochloric acid. In addition, the i.r. spectra of the mixed-ligand chelate shows the expected additional absorptions due to the carboxylate groups of edta or threonine. The mixed-ligand chelates of nickel(II) may be prepared in a similar manner (see Table 1). The absorption spectra of the mixed-ligand chelate of Cu^{II} with 3-hydroxyphenylrhodanine and threonine consists of a single, rather broad absorption centred close to 502 nm ($\varepsilon = 1.02 \times 10^4$ dm^3 mol^{-1} cm^{-1}).

TABLE 2

Magnetic parameters for the e.s.r. spectra

Chelate	$g_{\parallel}$	$g_{\perp}$	$10^4A_{\parallel}$/ cm^{-1}	$10^4A_{\perp}$/ cm^{-1}
(*a*) 3-Hydroxyphenylrhodanine chelates				
$Cu(L^1)_2 \cdot 2Me_2CO$	2.186 ± 0.005	2.04 ± 0.01	165 ± 5	20
$Cu(L^1)_2 \cdot 4py$	2.182 ± 0.005	2.04 ± 0.001	168 ± 5	20
(*b*) Mixed-ligand chelates *				
$Cu(ThrO)L^1$	2.209 ± 0.005	2.02 ± 0.01	170 ± 5	10
$Cu(H_2edta)(HL^1)$	2.209 ± 0.005	2.04 ± 0.01	168 ± 5	10

* In dmf–pyridine solution.

The formation of the mixed-ligand chelate in neutral or weakly acidic solution requires replacement of a proton from both ligands in the case of the threonine derivatives. In the case of the complexes involving edta, the mixed-ligand chelate is thought to form as a result of bonding of two carboxylate groups of the edta, with the remaining two carboxylate groups and the hydroxyl groups in the 3-hydroxyphenylrhodanine remaining un-ionised. Inclusion of sodium ion into the empirical formulae makes the agreement of the analytical results decidedly worse. The magnetic susceptibility measurements on the mixed-ligand chelates $Cu(ThrO)L^1$ and $Cu(H_2edta)(HL^1)$ give values of $\mu_{eff.}$ equal to 1.87 and 1.86 B.M. respectively (ThrO = threoninate). The mixed-ligand chelates, $Cu(ThrO)L^1$, $Cu(ThrO)(Thr)_{0.5}L^2$, $Cu(H_2edta)(HL^1)$, and $Cu(H_2edta)(HL^2)$ in dmf solution with 10% v/v of pyridine possess similar e.s.r. spectra at 77 K, a typical example of which is shown in Figure 4.

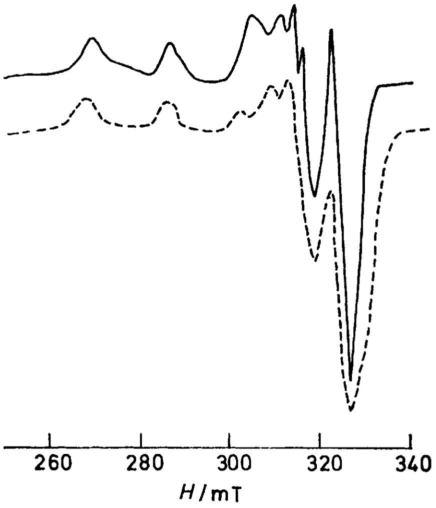

FIGURE 4 E.s.r. spectrum of the mixed-ligand chelate $Cu(ThrO)L^1$ in dmf solution containing 10% v/v of pyridine at 77 K. Dashed curve as in Figure 2

The magnetic parameters associated with the e.s.r. spectra shown in Figure 5 and that due to the mixed-ligand chelate, $Cu(H_2edta)(HL^2)$, were determined by computer simulation using the axial symmetric spin Hamiltonian described earlier. The results are summarised in Table 2.

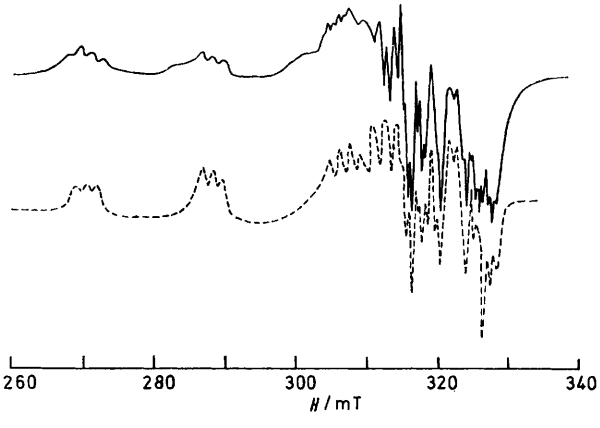

FIGURE 5 E.s.r. spectrum of the chelate $Cu(ThrO)L^1$ in dmf solution (5.0×10^{-3} mol dm^{-3}) at 77 K. The dashed curve shows the computer simulation using the parameters listed in the text

A solution of the chelate $Cu(ThrO)L^1$ in dmf at 77 K gave the e.s.r. spectrum depicted in Figure 5 which shows a further spectral type, the magnetic parameters being obtained by computer simulation involving the spin Hamiltonian as shown in equation (2) ($i = x, y, z$), which represents the central copper(II) in an orthorhombic distribution of ligand atoms. The spectrum shows extrahyperfine coupling due to an interaction of the unpaired

$$\mathscr{H} = \beta(g_xH_xS_x + g_yH_yS_y + g_zH_zS_z) + A_xS_xI_x + A_yS_yI_y + A_zS_zI_z + \Sigma A_i^{\mathrm{N}}S_iI_i^{\mathrm{N}} \quad (2)$$

electron of the copper(II) with the ^{14}N nucleus presumably associated with the threonine ligand. The values of the magnetic parameters obtained from the best fit of the experimental spectrum are as follows (g values are ± 0.001 throughout unless otherwise stated): $g_z = 2.187$, $g_y = 2.072$, $g_x = 2.015$; $A_z(^{63}\mathrm{Cu}) = (187 \pm 2) \times 10^{-4}$, $A_y(^{63}\mathrm{Cu}) = (13 \pm 2) \times 10^{-4}$, $A_x(^{63}\mathrm{Cu}) = (13 \pm 2) \times 10^{-4}$ cm^{-1}; $A_z(\mathrm{N}) = (15 \pm 1) \times 10^{-4}$, $A_y(\mathrm{N}) = (15 \pm 1) \times 10^{-4}$, $A_x(\mathrm{N}) = (15 \pm 1) \times 10^{-4}$ cm^{-1}.

Formation of the Dithiocarbamato-chelates.—The copper(II) chelates $\mathrm{Cu(L^1)_2 \cdot 2H_2O}$ and $\mathrm{Cu(L^2)_2 \cdot 2H_2O}$ dissolve readily in chloroform or methylene chloride; however, the colour of the solutions is changed from that of the chelates in acetone or dmf, this being due to a single, rather broad absorption band centred close to 440 nm ($\varepsilon = 1.03 \times 10^4$ dm^3 mol^{-1} cm^{-1}).

The e.s.r. spectra of samples of the solutions prepared by dissolution of the chelates $\mathrm{Cu(L^1)_2 \cdot 2H_2O}$ or $\mathrm{Cu(L^2)_2 \cdot 2H_2O}$ in chloroform recorded at 77 K are quite different from those of the chelates dissolved in solvents such as acetonitrile or dmf. The e.s.r. spectra due to these chloroform solutions are in fact quite like those of copper(II) diethyldithiocarbamates in organic solvents.[4] The elemental analysis of the products isolated from the chloroform solutions (Table 1), as well as a comparison of the i.r. spectra of the products with that of bis(diethyldithiocarbamato)copper(II), leads to the conclusion that the products are indeed thiocarbamates: namely, bis(*N*-chloroacetyl-*N*-3-hydroxyphenyldithiocarbamato)copper(II), designated $\mathrm{Cu(L^3)_2}$; and bis(*N*-chloroacetyl-*N*-4,5-dibromo-3-hydroxyphenyldithiocarbamato)copper(II), designated $\mathrm{Cu(L^4)_2}$. The copper(II) thiocarbamates when redissolved in chloroform solution gave the same e.s.r. spectra observed earlier on dissolution of the chelates $\mathrm{Cu(L^1)_2 \cdot 2H_2O}$ or $\mathrm{Cu(L^2)_2 \cdot 2H_2O}$ in chloroform.

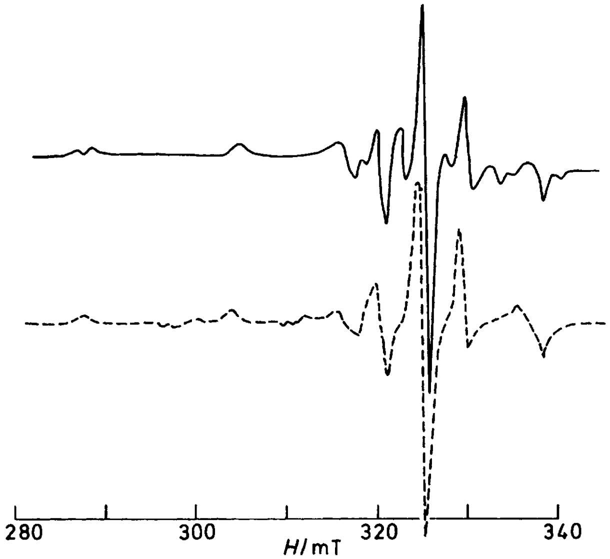

FIGURE 6 E.s.r. spectrum of the chelate $\mathrm{Cu(L^3)_2}$ in chloroform solution (5.0×10^{-3} mol dm^{-3}) at 77 K. Dashed curve as in Figure 5

The e.s.r. spectra of a chloroform solution of $\mathrm{Cu(L^3)_2}$ is shown in Figure 6. The conversion of the copper(II) rhodanine chelates into the appropriate copper(II) dithiocarbamates is complete even at room temperature. Computer simulation of the experimental e.s.r. spectra of the copper(II) dithiocarbamate $\mathrm{Cu(L^3)_2}$, and using the spin Hamiltonian appropriate to an orthorhombic distribution of ligand atoms, gives the following values of the magnetic parameters: $g_z = 2.098$, $g_y = 2.025$, $g_x = 2.020$; $A_z(^{63}\mathrm{Cu}) = (162 \pm 2) \times 10^{-4}$, $A_y(^{63}\mathrm{Cu}) = (42 \pm 2) \times 10^{-4}$, $A_x(^{63}\mathrm{Cu}) = (36 \pm 2) \times 10^{-4}$ cm^{-1}. There is sufficient resolution in the experimental spectra to discern the contribution to the spectra due to the ^{65}Cu isotope form of the chelate. The corresponding zinc(II) and nickel(II) chelates of 3-hydroxyphenylrhodanine are not converted into dithiocarbamate after treatment with chloroform, while the chelate $\mathrm{Cu(HL^1)_2(NO_3)_2}$ is unaffected by chloroform. The mixed-ligand chelates described earlier are insoluble in chloroform. Bearing in mind that the synthesis of the 3-hydroxyphenylrhodanine involves as a first step the synthesis of *N*-3-hydroxyphenyldithiocarbamate, the copper(II) chelate of this ligand was prepared; the analytical data are in Table 1. The e.s.r. spectra due to the copper(II) chelate of *N*-3-hydroxyphenyldithiocarbamate in dmf solution are shown in Figure 7. The chelate does not dissolve in chloroform. The magnetic parameters appropriate to the e.s.r. spectrum in Figure 7 are as follows: $g_z = 2.096$, $g_y = 2.027$, $g_x = 2.025$; $A_z = (154 \pm 2) \times 10^{-4}$, $A_y = (40 \pm 2) \times 10^{-4}$, $A_x = (34 \pm 2) \times 10^{-4}$ cm^{-1}.

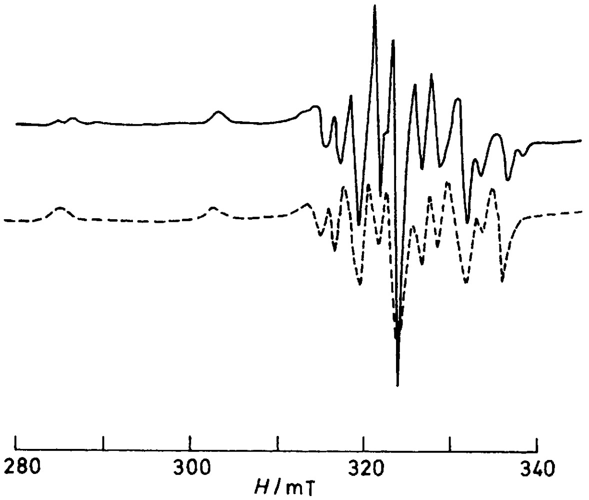

FIGURE 7 E.s.r. spectrum of the chelate bis(*N*-3-hydroxyphenyldithiocarbamato)copper(II) in dmf solution (5.0×10^{-3} mol dm^{-3}) at 77 K. Dashed curve as in Figure 5

DISCUSSION

The formation of the highly coloured copper(II) chelates of 3-hydroxyphenylrhodanine and its dibromoderivative proceeds by bonding with the deprotonated hydroxyl group and co-ordination with the C=S group of the rhodanine ring. The e.s.r. spectral data show that in the tetrapyridine solvate of the chelate each of the pyridine molecules is co-ordinated to the copper(II), which retains co-ordination by the C=S group but releases the deprotonated hydroxyl group.

There are numerous examples of the formation of mixed-ligand chelates of copper(II) described in the literature.[5,6] Indeed, with particular reference to the present work, the formation of mixed-ligand chelates of copper(II) with amino-acids and certain 3,4-dihydroxyphenols has been described.[7]

The e.s.r. spectrum of the mixed-ligand chelate Cu(ThrO)L[1] in dmf is closely similar to that observed for copper(II) chelates of ligands formed from the thiosemicarbazones of salicylaldehyde and its derivatives.[8] The donor set of atoms from the ligand in these phenolic thiosemicarbazone ligands is O_2NS with one of the oxygen atoms coming from a co-ordinated water molecule. The similarity of the e.s.r. spectra of the mixed-ligand chelates studied here presumably arises from the presentation of a similar donor set of atoms with the sulphur supplied by the C=S group of the rhodanine, and nitrogen and oxygen from the amino-acid.

The ready conversion of the copper(II) chelate of 3-hydroxyphenylrhodanine or its dibromo-derivative in chloroform or methylene chloride solution is an unusual reaction, proceeding presumably *via* carbonium ion and also sulphide formation after heterolytic cleavage of the $-CH_2-S-$ linkage. The copper(II) atom lies quite close for ultimate bonding to the dithiocarbamate group. Subsequent changes involve the acquisition of chloride from the chloroform, and hydrogen ion by the ionised phenolic group, formerly bound to the copper(II). The reasons which enable the ring fission to take place remain obscure, however it is of interest to note that a quite similar process which results in the formation of the dithiocarbamate ion provides the fungitoxicity properties of certain rhodanine derivatives under physiological conditions. The conversion of the copper(II) chelates of 3-hydroxyrhodanine into the thiocarbamato-chelate is unfortunately restricted to copper(II), however it does provide an opportunity to obtain the copper(II) chelate of a dithiocarbamate with highly unsymmetrical groups attached to the nitrogen atom of the ligand.

EXPERIMENTAL

The e.s.r. spectra were recorded at 77 K using the *X*-band of a Varian E12 spectrometer with $\nu = 9\ 149$ MHz. Infrared spectra were obtained on a Perkin-Elmer model 521 spectrophotometer with sodium chloride optics, visible absorption spectra on a Unicam SP 700 spectrophotometer. Magnetic susceptibility measurements were made at room temperature by the Gouy method with a glass tube calibrated for diamagnetism. All organic solvents were freshly distilled before use and dried over Linde 4A molecular sieves.

Preparation of 3-Hydroxyphenylrhodanine.—3-Hydroxyphenylrhodanine was prepared by the method outlined by Brown *et al.*[9] The synthesis comprises two steps, the first involving the formation of the thiocarbamate derived from 3-hydroxyaniline, followed by a cyclisation reaction using sodium chloroacetate to form the rhodanine derivative. To a mixture of carbon disulphide (18.9 g) and concentrated aqueous ammonia (50 cm^3), cooled in ice, was added 3-hydroxyaniline (28 g) in small quantities over a period of 20 min with continuous stirring. The ammonium salt of the resulting dithiocarbamate precipitated after allowing the reaction mixture to stand overnight. An aqueous solution of sodium chloroacetate was prepared by mixing ice-cold solutions of chloroacetic acid (19 g) and sodium hydroxide (7 g) each in water (25 cm^3). The resultant mixture was treated with anhydrous sodium carbonate until the aqueous solution was just alkaline. The ammonium salt of the thiocarbamate isolated previously was added to the ice-cooled solution of sodium chloroacetate over a 15-min period with continuous stirring. The light yellow product which separated from solution was filtered off, treated with dilute hydrochloric acid (70 cm^3 concentrated hydrochloric acid–30 cm^3 water), and heated to 85—90 °C for 20 min. On cooling, the resultant crystalline product was washed with water and recrystallised from acetone. The 4,5-dibromo-derivative was obtained from Maybridge Chemical Co. Ltd.

Preparation of Metal Chelates of 3-Hydroxyphenylrhodanine.—The copper(II), zinc(II), and nickel(II) chelates were prepared by the addition of an acetone solution (50 cm^3) of 3-hydroxyphenylrhodanine (20 mmol) containing triethylamine (20 mmol) to an aqueous solution (50 cm^3) of the metal nitrate (10 mmol). Chelates of the 4,5-dibromo-derivative were prepared in the same way. The resulting products were washed well with water. Recrystallisation from acetone or pyridine yielded the solvates of the chelates.

Preparation of the Mixed-ligand Chelates.—In a typical procedure an aqueous solution (50 cm^3) containing copper(II) nitrate (10 mmol) and threonine (20 mmol) at pH *ca.* 7 was treated with an acetone solution (50 cm^3) of 3-hydroxyphenylrhodanine (10 mmol). A dark brown precipitate of the mixed-ligand chelate separated from solution, yield 70%.

Conversion of the Copper(II) *Chelates of 3-Hydroxyphenylrhodanine into Copper*(II) *Thiocarbamate Chelates.*—The copper(II) chelate of 3-hydroxyphenylrhodanine was dissolved in freshly distilled chloroform which had been previously washed with aqueous sodium bicarbonate solution to remove any mineral acid content. After standing for *ca.* 1 h the solvent was distilled off at diminished pressure to yield the copper(II) dithiocarbamate.

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