STUDY ON SEMI-GLYCINECRESOL RED COMPLEXES WITH BIVALENT METAL IONS

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Summary—Semi-Glycinecresol Red (SGCR or H_3SGCR) was purified by means of chromatography on cellulose and by cation-exchange. A potentiometric, spectrophotometric and ESR study on the complex formation equilibria of several bivalent metal ions with SGCR was performed. The acid–base and metal–ligand stoichiometries were determined, and the formation constants, λ_{max} and absorptivities of the visible-region absorption spectra of the corresponding proton and metal complexes were determined. The copper complexes were examined by ESR spectroscopy. Each metal ion was found to form the 1:1 and 1:2 (metal:ligand) complex species, $MSGCR^-$ and $M(SGCR)_2^{4-}$, in alkaline solution. However, only Cu(II) was found to form the protonated complexes, $CuHSGCR$ and $Cu(HSGCR)_2^{2-}$, in weakly acidic media. SGCR is suitable as an indicator for Cu(II) in a weakly acidic solution and for Cu(II), Zn(II) and Pb(II) in alkaline solution

Semi-Glycinecresol Red (SGCR or H_3SGCR), 3-(N-carboxymethylaminomethyl-o-cresolsulphonephthalein, which is shown in formula (I), is thought to be produced in the course of synthesis of Glycinecresol Red, 3,3′-bis(N-carboxymethylaminomethyl)-o-cresolsulphonephthalein. SGCR has not hitherto been purified, hence its physico-chemical properties such as the stoichiometry stabilities and visible-region absorption spectra of its complexes, which are important factors in its analytical application as an indicator, are not known in detail.

In the present work, SGCR was synthesized and purified by means of chromatography on cellulose and by cation-exchange, and the value of SGCR as an indicator for titration of several bivalent metal ions was investigated potentiometrically, spectrophotometrically and by ESR spectrometry.
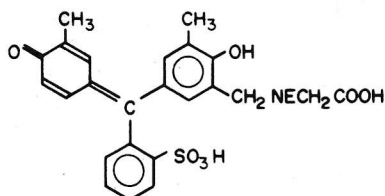
(I) SGCR

EXPERIMENTAL

Reagents

SGCR. SGCR was synthesized[1] and purified by means of cellulose column chromatography[2] with n-butanol saturated with 5% acetic acid solution and by batchwise ion-exchange.[3] The purity of the SGCR was established by elemental analysis, potentiometric titration, paper chromatography and absorption spectra (found: C, 58.8%; H, 5.1%; N, 2.8%; calculated for $C_{24}H_{23}O_7NS \cdot H_2O$: C, 59.12%; H, 5.17%; N, 2.87%).

Stock solutions of metal ions, 0.01 M. Prepared by dissolving analytical-reagent grade metal nitrates in pure water, and standardized with EDTA. The solutions were diluted to the desired concentration with pure water.

Apparatus

Visible spectrophotometry and pH-titrations were performed as described previously.[3] Concentrations of SGCR used were $1.0 \times 10^{-3}M$ for pH-titration and $1.0 \times 10^{-5}M$ for visible-region spectral measurements, and the concentrations of the metal ions were varied according to the desired mole ratio.

ESR. ESR spectra of the Cu(II) complexes were recorded with a JEOL JES-ME X-band spectrometer with 100-kHz modulation and the field was calibrated with Mn^{2+}-doped magnesium oxide powder. The measurements were carried out in solution at 298 K and in frozen media at 77 K. The quartz sample tubes were 1 and 4 mm in internal diameter for the measurements at 298 and 77 K respectively. The solvents were water at 298 K, and water–ethylene glycol mixture (1:1 v/v) at 77 K. The pH was adjusted with sodium hydroxide and perchloric acid. The concentration of Cu(II) was $5.0 \times 10^{-3}M$ and that of SGCR was varied according to the mole ratio desired.

RESULTS AND DISCUSSION

Acid dissociation equilibrium and optical constants of SGCR

These were determined as described previously[2] and the values are summarized in Tables 1 and 2, respectively. Consideration of the acid formation and

Table 1. Acid formation constants of SGCR at 25°C and $\mu = 0.1$ (KNO$_3$)

| $\log k_1$	$\log k_2$	$\log k_3$	$\log k_4$	$\log k_5$
10.07	7.44*	2.47*	−0.27	−1.76

* Measured by pH-titration, the rest by spectrophotometry at room temperature.

optical constants suggests that k_1, k_2, k_3, k_4 and k_5 correspond to protonation of the imino, phenolic, carboxylic, quinone and sulphonic groups respectively.[2]

Complex formation equilibria

Cu(II) complexes. The titration curves will be referred to as the "1/1" and "1/2" curves, corresponding to titrations of SGCR when the mole ratio of Cu(II): SGCR is 1:1 and 1:2 respectively. The 1/1 curve (Fig. 1) shows two well-defined inflection points at $a = 2$ and $a = 3$ (where a is number of moles of base added per mole of SGCR), indicating the following equilibria involved in the solution.

$a = 0$–2:

$$Cu^{2+} + H_3SGCR \rightleftharpoons CuHSGCR + 2H^+$$

$a = 2$–3:

$$CuHSGCR \rightleftharpoons CuSGCR^- + H^+$$
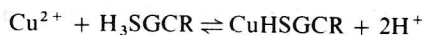
The 1/2 curve in Fig. 2 shows three inflections at $m = 3$, 4 and 6 (where m is number of moles of base added per mole of metal ion), although these inflections are not so well-defined as those of the 1/1 curve. The buffer region between $m = 3$ and 4 was at almost the same pH as that between $a = 2$ and 3 for the 1/1 curve. Therefore, CuHSGCR, which is formed below $m = 3$, may dissociate a proton. The pH of the buffer region between $m = 4$ and 6 was almost identical to that between $a = 1$ and 2, in which a

Table 2. Wavelengths of maximum absorbance and molar absorptivities of ligand and complex species for SGCR at room temperature and $\mu = 0.1$ (KNO$_3$)

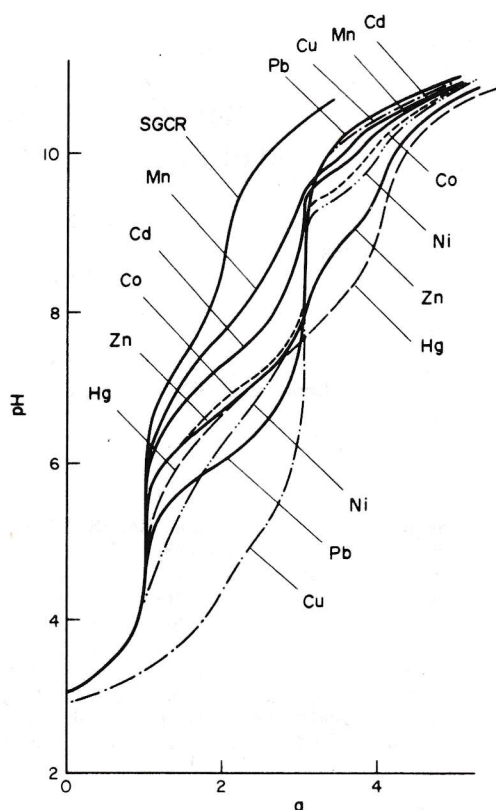| Species	λ_{max}, nm	Absorptivity, 10^4 l.mole^{-1}.cm^{-1}
L^{3-}	582	6.76
HL^{2-}	578	6.42
H_2L^-	442	2.69
H_3L	442	2.69
H_4L^+	518	4.16
H_5L^{2+}	518	6.78
MnL^-	575	4.38
CoL^-	577	4.45
NiL^-	580	5.77
CuL^-	538	3.45
$CuHL$	475	2.41
ZnL^-	540	3.75
CdL^-	574	5.31
PbL^-	523	2.75
$Ni(OH)L^{2-}$	550	4.32
	587	4.87
$Pb(OH)L^{2-}$	577	4.72

Fig. 1. Titration curves of $1 \times 10^{-3} M$ SGCR solutions containing 1:1 molar ratio of metal ion to SGCR, at 25°C and $\mu = 0.1$ (KNO$_3$). a = number of moles of base added per mole of SGCR.
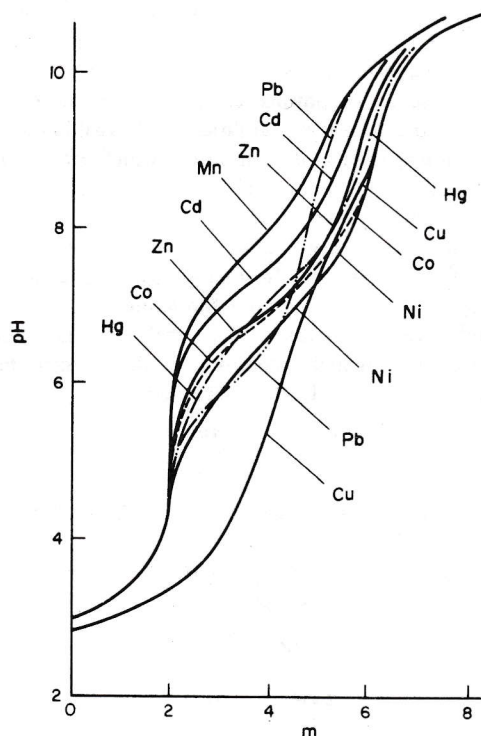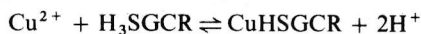

Fig. 2. Titration curves of $1 \times 10^{-3} M$ SGCR solutions containing 1:2 mole ratio of metal ion to SGCR, at 25°C and $\mu = 0.1$ (KNO$_3$). m = number of moles of base added per mole of metal ion.

free H_2SGCR^- may dissociate a proton and then the free $HSGCR^{2-}$ may react with $CuSGCR^-$ to form the 1:2 complex species $Cu(SGCR)_2^{4-}$ (hereafter, the complexes with 1:1 and 1:2 mole ratios of metal ion to SGCR are referred to as the "1:1" and "1:2" complexes). The reactions involved in the 1/2 solution are probably as follows.
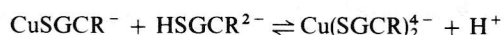
$m = 0-3$:

$$Cu^{2+} + H_3SGCR \rightleftharpoons CuHSGCR + 2H^+$$

$$H_3SGCR \rightleftharpoons H_2SGCR^- + H^+$$

$m = 3-4$:

$$CuHSGCR \rightleftharpoons CuSGCR^- + H^+$$

$m = 4-6$:

$$H_2SGCR^- \rightleftharpoons HSGCR^{2-} + H^+$$

$$CuSGCR^- + HSGCR^{2-} \rightleftharpoons Cu(SGCR)_2^{4-} + H^+$$

The visible absorption spectra of the 1/1 Cu(II) solution at various pH values showed the complex-formation behaviour assumed from the potentiometric titration. However, the spectra of the 1/2 solutions were very broad, indicating that many reactions were involved, and the stoichiometries of the complexes were difficult to determine from these spectra.

ESR spectra of the frozen 1/1 and 1/5 Cu(II) solutions at 77 K are shown in Fig. 3. As seen in spectra 1 and 2, at pH 4 (which corresponds to the pH-value at $a = 2$ on the 1/1 titration curve and $m = 3$ on the 1/2 titration curve) three kinds of Cu(II) species are detected, with spectra indicated by (a), (b) and (c) [(b) in spectrum 1 is the same as (b) in spectrum 2]. The ESR spectra will be discussed later in detail. Spectrum (a) is probably that of the aquated Cu(II) ion. From the pH-titration, (b) may be attributed to the complex species CuHSGR. The third complex, indicated by (c), is not detected from the pH-titrations and the visible-region absorption spectra, and is probably the 1:2 complex species $Cu(HSGCR)_2^{2-}$.
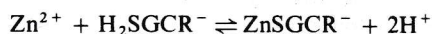
The spectra of the 1/1 and 1/5 solutions at pH 7 were also quite similar and may be attributed to the complex $CuSGCR^-$. The spectrum of the 1/1 solution at pH 10 is akin to that recorded at pH 7. The spectrum of the 1/5 solution shows the overlapping hyperfine spectra of probably two complex species, with two different A splittings, indicated by (d) and (e). The spectrum (d) is identical in 4 and 5 and may be attributed to the same complex species, so spectrum (e) is probably attributable to the complex $Cu(SGCR)_2^{4-}$. Although these protonated complexes cannot be deduced from the pH-titration curves and visible-region spectra at pH < 4 the ESR spectra show them to be formed at pH nearly down to 3.

The visible-region absorption spectra became similar to that of SGCR above pH $ca.$ 11 for the 1/1 and pH $ca.$ 12 for the 1/2 solutions and the ESR spectra became similar to that of the tetrahydroxocuprate ion, $Cu(OH)_4^{2-}$, above pH $ca.$ 11 for the 1/1 and pH $ca.$ 12.5 for the 1/5 solutions. These findings

suggest that the complex species $CuSGCR^-$ and $Cu(SGCR)_2^{4-}$ may dissociate to give the free $Cu(OH)_4^{2-}$ ion and $SGCR^{3-}$. Signs of a hydroxo complex of Cu(II) and SGCR could not be detected in the visible-region and ESR spectra.

Other metal complexes. The 1/1 curves for Zn(II), Ni(II), Co(II), Cd(II) and Mn(II) have three inflection points at $a = 1$, $a = 3$ and $a = 4$ as seen in Fig. 1, and the curves between $a = 0$ and $a = 1$ are identical to the titration curve of SGCR, indicating that these metal ions do not react with SGCR at pH below 5. Further addition of base beyond $a = 3-4$ results in a white precipitate of the metal hydroxide, and therefore the following reactions probably occur after $a = 1$.

$a = 1-3$:

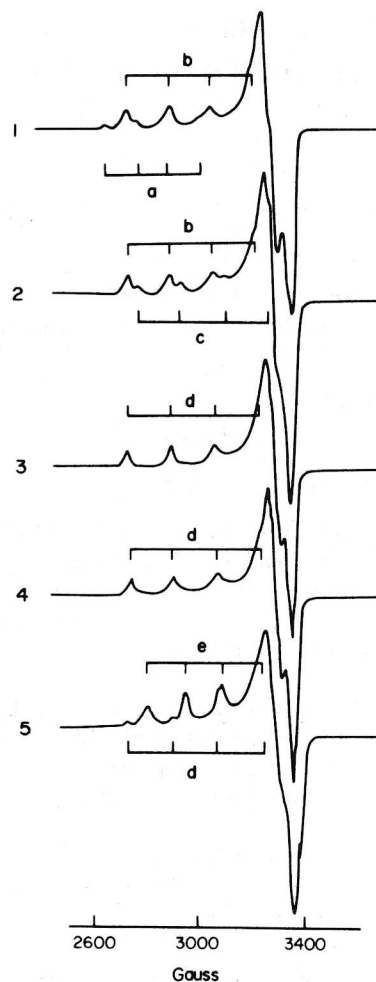$$Zn^{2+} + H_2SGCR^- \rightleftharpoons ZnSGCR^- + 2H^+$$

$a = 3-4$:

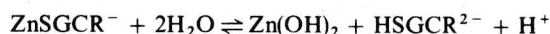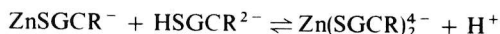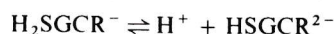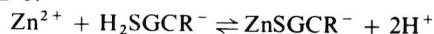$$ZnSGCR^- + 2H_2O \rightleftharpoons Zn(OH)_2 + HSGCR^{2-} + H^+$$

Fig. 3. First-derivative ESR spectra of the Cu(II) and SGCR solutions (at 77 K) at various pH values and mole ratios. Cu(II): 5×10^{-3} M. Mole ratio of Cu(II) to SGCR: 1–1/1, 2–1/5, 3–1/1 and 1/5 (spectra identical), 4–1/1, 5–1/5. pH: 1 and 2–4.0, 3–7.0, 4 and 5–10.0.

The 1/1 Pb(II) curve has two inflections at $a = 1$ and $a = 3$, and the shape of the curve between them is similar to that for Zn(II) but there is no visible inflection at $a = 4$. Thus the behaviour of Pb(II) is similar to that of Zn(II) below $a = 3$, and to that of Cu(II) above $a = 3$.

The 1/1 Hg(II) curve has a long sloping buffer region between $a = 1$ (pH 5) and $a = 4$ (pH 9), where a white precipitate is formed, and this may indicate that formation and hydrolysis of the complex overlap, production of the species $Hg(OH)_2$ and $HSGCR^-$ being complete at $a = 4$, liberating three moles of protons per mole of SGCR in this buffer region.

The 1/2 curves for Zn(II), Co(II), Ni(II) and Cd(II) have two inflections at $m = 2$ and $m = 6$. In the long buffer region in between, first the 1:1 and then the 1:2 complex species may be formed. The reactions are probably the following.

$m = 2$–6:

$$Zn^{2+} + H_2SGCR^- \rightleftharpoons ZnSGCR^- + 2H^+$$

$$H_2SGCR^- \rightleftharpoons H^+ + HSGCR^{2-}$$

$$ZnSGCR^- + HSGCR^{2-} \rightleftharpoons Zn(SGCR)_2^{4-} + H^+$$

The 1/2 Pb(III) and Mn(II) curves have two inflections at $m = 2$ and $m = 5$. The reactions involved are

$m = 2$–5:

$$Pb^{2+} + H_2SGCR^- \rightleftharpoons PbSGCR^- + 2H^+$$

$$H_2SGCR^- \rightleftharpoons HSGCR^{2-} + H^+$$
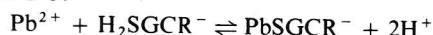
and the formation of the 1:2 complex would probably occur at higher pH after $m = 5$, the reactions perhaps being

$m > 5$:

$$HSGCR^{2-} \rightleftharpoons SGCR^{3-} + H^+$$

$$PbSGCR^- + SGCR^{3-} \rightleftharpoons Pb(SGCR)_2^{4-}$$

The 1/2 Hg(II) curve has a long buffer region between $m = 2$ and $m = 6$, and then a white precipitate appears. The reactions in the Hg(II) solution probably involve the successive formation of the 1:1 complex then and 1:2 complexes, and finally hydrolysis.

The visible-region spectra of the 1/1 and 1/2 solutions showed changes at two pH-values corresponding to those of the buffer region of the pH-titration, where the formation and the hydrolysis of the com-

plexes $MSGCR^-$ and $M(SGCR)_2^{4-}$ occurred. In alkaline solution, the spectra of the Zn(II), Cd(II), Co(II) and Mn(II) systems showed no evidence of hydroxo complexes or direct dissociation to $M(OH)_2$ and ligand. However, the spectra for the Pb(II) and Ni(II) systems showed two reactions, indicating existence of the hydroxo complexes[4] $Pb(OH)L^{2-}$ and $Ni(OH)L^{2-}$ and their dissociation to $M(OH)_2$ (precipitated) and SGCR at pH above 12. The spectrum corresponding to $Ni(OH)L^{2-}$ had two absorption maxima at 550 and 587 nm, but that for $Pb(OH)L^{2-}$ had only one maximum.

The optical constants for the metal complexes of SGCR are summarized in Table 2; those for the 1:2 complexes were difficult to determine because the complexation reactions are so complicated.

Formation constants of the metal complexes of SGCR are listed in Table 3. They were calculated by an adaptation[4] of Bjerrum's method. The constants K_{MHL} for CuHSGCR and $K_{M(OH)L}$ for $Pb(OH)SGCR^{2-}$ and $Ni(OH)SGCR^{2-}$ were obtained graphically from the plots of $\log[MHL]/[ML]$ and $\log[ML]/[M(OH)_nL]$ *vs.* pH or pOH by the methods previously described.[5]

ESR spectra and parameters

The ESR spectra of the 1/1 Cu(II) and SGCR solution at pH 7.0 are shown in Fig. 4. The spectra 1, 2 and 3 may be assigned to the complex species $CuSGCR^-$, as discussed above. The spectrum recorded at 298 K shows four lines of the isotropic hyperfine structure from the copper nucleus. However, two lines in the lower field are poorly resolved. At temperatures above 327 K their resolution is much improved and the isotropic hyperfine splitting A_0 was obtained accurately. This means that the molecule of SGCR is large and the molecular tumbling of the complex is slow at room temperature, hence the anisotropic coupling is not averaged out completely.[6]

The spectrum at 77 K shows the well-defined copper hyperfine coupling lines A_z parallel to the external magnetic field direction, defined here as the direction of the Cartesian z-axis. However, the fourth line in the highest field is observed as a shoulder overlapped on the $g_\perp$ structure for the components perpendicular to the external magnetic field. These lines in the highest field are shown in spectrum 3. Several of the lines are not well resolved. These lines may be ascribed to the anisotropic hyperfine splitting, A_x and A_y, as

Table 3. Formation constants of complexes at 25°C and $\mu = 0.1$ (KNO$_3$)

Ligand	Reaction		Mn	Co	Ni	log K Cu	Zn	Cd	Pb
SGCR	$M^{2+} + L^{3-} \rightleftharpoons ML^-$	K_{ML}	4.6	7.6	8.8	12.8	7.6	6.2	9.1
	$ML^- + L^{3-} \rightleftharpoons ML_2^{4-}$	K_{ML_2}	3.1	5.4	6.1	5.2	5.7	4.3	3.4
	$ML^- + H^+ \rightleftharpoons MHL$	K_{MHL}				5.3			
	$ML^- + OH^- \rightleftharpoons M(OH)L^{2-}$	$K_{M(OH)L}$			3.8*				4.0*

* Measured by spectrophotometry at room temperature; the rest by pH-titration.

The anisotropic g-factors, g_x and g_y, and hyperfine constants, $|A_x|$ and $|A_y|$, are almost equal. This indicates that the Cu(II) complexes with SGCR have almost axial symmetry. Therefore, if the Cu(II) complexes have axial symmetry D_{4h}, the following equations would hold:

$$g_z = g_\parallel; \quad A_z = A_\parallel$$
$$g_\perp = (g_x + g_y)/2; \quad A_\perp = (A_x + A_y)/2 \quad (1)$$

where $g_\parallel$, $A_\parallel$, $g_\perp$ and $A_\perp$ are the components of the anisotropic g-factor and hyperfine constant parallel to and perpendicular to the static magnetic field.

If the ligand field transition energies are estimated from the visible-region absorption spectra, the LCAO–MO parameters of the antibonding orbitals in the Cu(II) paramagnetic site can be determined and detailed discussion on the nature of the chemical bond is possible. However, the spectrum arising from the d–d electron transition of Cu^{2+} is overlapped by the absorption spectrum of SGCR. Therefore, only the LCAO–MO coefficient, α, of the antibonding orbital $\psi_{B_{1g}}$ [equation (2)] was calculated from equation (3).

$$\psi_{B_{1g}} = \alpha d_{x^2-y^2} - \alpha'(-\sigma_x^{(1)} + \sigma_y^{(2)} + \sigma_x^{(3)} - \sigma_y^{(4)})/2 \quad (2)$$
$$\alpha^2 = \frac{A_\parallel}{P} + (g_\parallel - 2.0023) + \frac{3}{7}(g_\perp - 2.0023) + 0.04 \quad (3)$$

The symbols in equations (2) and (3) are those described in the literature.[7] B_{1g} represents in-plane σ-bonding and the four donor atoms on the x and y axes are labelled by superscripts starting with (1) for the x axis and proceeding counter-clockwise. The σ-orbitals are hybridized sp^2 orbitals of the donor atoms. For free Cu(II), P has the value -0.036 cm^{-1}. $A_\parallel$ usually has a negative sign and its value in gauss is converted into frequency units from the equation

$$A(\text{cm}^{-1}) = 4.669 \times 10^{-5} \, gA \text{ (gauss)}$$

The $g_\perp$ and $A_\perp$ values for CuHSGCR and $Cu(SGCR)_2^{4-}$ were calculated from the equations $g_0 = (g_\parallel + 2g_\perp)/3$ and $A_0 = (A_\parallel + 2A_\perp)/3$, and are given in parentheses in Table 4.
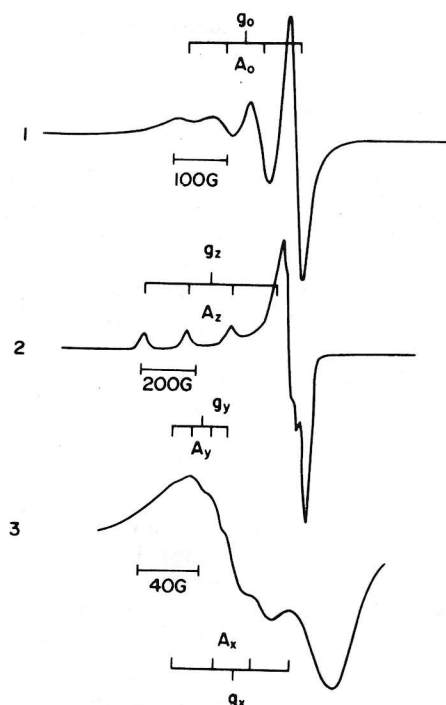

Fig. 4. First-derivative ESR spectra of Cu(II) and SGCR solutions at pH 7.0. Cu(II): $5 \times 10^{-3} M$, SGCR: $5 \times 10^{-3} M$. Temperature: 1–25°C, 2 and 3–77 K.

indicated in Fig. 4. Each anisotropic g-factor, $g_i(i = x, y$ or $z)$ for the three Cartesian axes, was determined from the centre of the corresponding hyperfine splitting and each anisotropic hyperfine constant $A_i(i = x, y, z)$ was determined from averaging the splitting widths of the four lines in spectra 2 and 3. The isotropic g-factor and hyperfine constant, g_0 and A_0, were determined similarly from spectrum 1. These values are tabulated in Table 4 together with those for the other complex species. The average values of the anisotropic constants $g_0 = (g_x + g_y + g_z)/3$ and $A_0 = (A_x + A_y + A_z)/3$ obtained from the spectra of CuSGCR$^-$ at 77 K show excellent agreement with the values of the isotropic constants, g_0 and A_0, obtained from the ESR measured at 298 K.

The ESR parameters for the other complex species were determined in the same manner as described above.

Table 4. ESR parameters of Cu(II)–SGCR complexes*

Species	g_0	g_x	g_y	g_z	A_0†	A_x†	A_y†	A_z†	α^2
CuHSGCR	2.141	(2.072)		2.279	66	(21)		156	0.81
Cu(HSGCR)$_2^{2-}$				2.245				154	
CuSGCR$^-$	2.139	2.063	2.079	2.276	67	26	13	162	0.82
Cu(SGCR)$_2^{4-}$	2.128	(2.064)		2.257	59	(19)		140	0.73

* Values omitted were difficult to determine because more than one complex was present and the spectra overlapped. The values in parentheses represented the mean values of the x- and y-axis components calculated by substituting the other known values into the equation $g_0 = (g_x + g_y + g_z)/3$ or $A_0 = (A_x + A_y + A_z)/3$.
† Measured in gauss.

The value of α^2 is lower for $Cu(SGCR)_2^{4-}$ than $CuSGCR^-$. This trend suggests that a decreasing axial ligand field causes an increase in strength of the in-plane σ-bonding. Hathaway and Billing[8] have discussed the concept of tetragonality, T, which is defined as equal to R_s/R_1, where R_s and R_1 are the short and long copper–ligand distances, respectively, and it can be related to the energy of the lowest electronic transition. Pradilla-Sorzanvo and Fackler[9] have discussed in-plane σ-bonding character in terms of tetragonality, T, and indicated that T decreases with decrease in α. This trend, observed for $CuSGCR^-$ and $Cu(SGCR)_2^{4-}$ suggests that the same tetragonal distortion probably occurs in these complexes. The α-value of $Cu(HSGCR)_2^{2-}$ could not be determined because the g_0 and A_0 values were difficult to determine, but g_z and A_z showed the same trend as in $Cu(SGCR)_2^{4-}$ and suggest that the tetragonality T decreases.

Colour change in complex formation

The colour change of an indicator in complex formation is one of the most important factors in its analytical application. The visible-region absorption spectra of the SGCR complexes may be attributed to the electronic $\pi-\pi^*$ transition characteristic of the sulphonephthalein group of the SGCR molecule and the change in colour may result from dissociation of protons or the coordination of the phenolic oxygen atom to the metal ion. The greater the colour change on the complex formation, the more useful the practical application. The wavelength shifts for the absorption maximum when the 1:1 complexes $MSGCR^-$ are formed from the species $SGCR^{3-}$ are plotted in Fig. 5 against the quantity $E_n^{\neq}$ introduced by Klopman[10] as a measure of the "hardness" of metal ions. The higher $E_n^{\neq}$, the harder the metal ion and the greater its affinity for hard donor atoms.[10,11] The
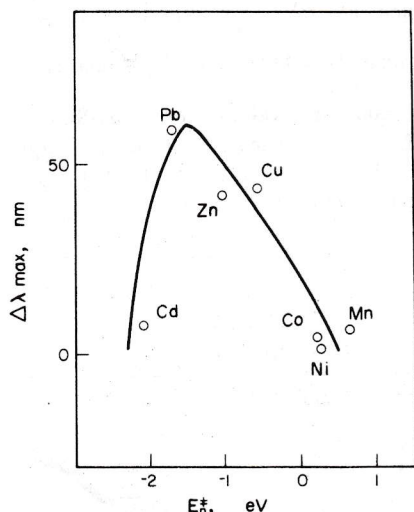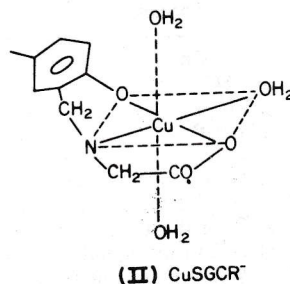
shift in λ_{max} arises from the combination of the localization of π-electron density on the phenolic oxygen atom by the inductive effect of the positively-charged metal ion and/or charge-transfer from the π-electron into the covalent bonding orbital between the phenolic oxygen atom and the metal ion. The extent of the first of these interactions would be increased by increase in the hardness. The value of $\Delta\lambda_{max}$ is maximal at $E_n^{\neq}$ ca. -1.5 eV because at higher or lower $E_n^{\neq}$ values there is a decrease in the ionic and covalent interactions respectively. Thus in terms of colour change, SGCR is most suitable for Pb(II), Zn(II) and Cu(II), which have $E_n^{\neq}$ values ranging from -1.5 to -0.5 eV.

### Formation constants and structures of the complexes

The relative values of the formation constants for the 1:1 complexes, $MSGCR^-$, show similar trends to those for a wide variety of ligands having oxygen and/or nitrogen donor atoms, the sequence usually being Mn(II) < Co(II) < Ni(II) < Cu(II) > Zn(II) and Cd(II) < Pb(II). It is noteworthy that the 1:1 Cu(II) complex with SGCR is especially stable. However, the formation constants for the 1:2 complexes of Cu(II) and Pb(II) do not follow the sequence above. This may be explained in terms of the co-ordination number of the metal ion. The $\log K_{ML_2}/\log K_{ML}$ ratios are about 0.7, 0.7, 0.7, 0.4, 0.7, 0.7 and 0.4 for Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) respectively. These metals may be divided into two groups according to these ratios. Cu(II) and Pb(II) are in one group and Mn(II), Co(II), Ni(II), Zn(II) and Cd(II) in the other. The co-ordination numbers, CN, of these metal ions in solution are usually 4 or 6. SGCR has three donor atoms, i.e., carboxylic oxygen, phenolic oxygen and imino nitrogen, and therefore, the co-ordination of two SGCR molecules to a metal ion would produce two patterns of behaviour for the formation constants of the 1:2 complexes according to whether the CN was 4 or 6. The ratio $\log K_{ML_2}/\log K_{ML}$ for a metal ion with CN 4 would be smaller than that for the a metal ion with CN 6 with respect to the terdentate ligand, SGCR, From this point of view, the CN may be 6 for Mn, Co, Ni and Zn and 4 for Pb and Cu. From the discussion above of the tetragonality, T, the in-plane σ-bonding in $Cu(SGCR)_2^{4-}$ is assumed to be increased and the co-ordination distance on the z-axis to be elongated, indicating that the Jahn–Teller stabilization increases.

Fig. 5. Plots of $\Delta\lambda_{max}$ for the complex $MSGCR^-$ vs. $E_n^{\neq}$ for the metal ion. $\Delta\lambda_{max}$ = difference between λ_{max} for the complex $MSGCR^-$ and for $SGCR^{3-}$. $E_n^{\neq}$ = hardness of metal ion, 10 eV.

(II) $CuSGCR^-$

However, the stability constant decreases. Therefore, the co-ordination sites on the elongated axis in $Cu(SGCR)_2^{4-}$ are assumed not to be occupied by the donor atoms of SGCR and the structures for $CuSGCR^-$ and $Cu(SGCR)_2^{4-}$ are assumed to be (II) and (III) respectively.

(III) $Cu(SGCR)_2^{4-}$
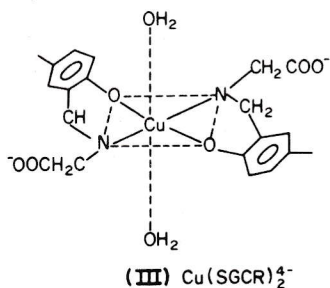
The relatively small value of log K_{ML_2}/log K_{ML} for Pb(II) is probably due to the tetragonal structure, which is frequently encountered in Pb(II) complexes in aqueous solution. The elongation of one bonding axis in $Cu(HSGCR)_2^{2-}$ is also indicated by the values of the ESR parameter, g_z and A_z. The dissociation of a proton from CuHSGCR to form $CuSGCR^-$ is accompanied by a colour change (λ_{max} changes from 475 to 538 nm). This suggests that the proton of CuHSGCR may be attached to the phenolic oxygen atom and the structure of CuHSGCR may be assumed to be (IV). There are no data for the visible-region absorption spectrum for $Cu(HSGCR)_2^{2-}$, but the proton may again be attached to the phenolic oxygen atom, in acidic media (pH ca. 4) and the structure is probably (V).

(IV) CuHSGCR

(V) $Cu(HSGCR)_2^{2-}$
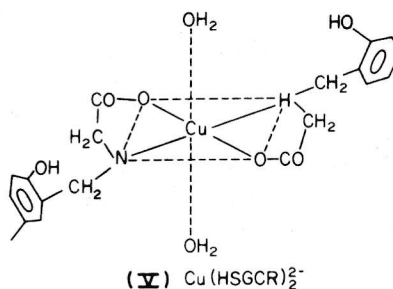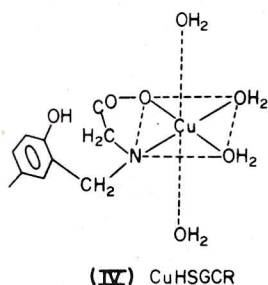
CONCLUSION

Only Cu(II) among the bivalent metal ions investigated here reacts with SGCR in a weakly acidic solution (pH ca. 4–6), so SGCR is available as the specific indicator for Cu(II) in such media. In alkaline solution, the colour change is large for formation of the Pb(II), Zn(II) and Cu(II) complexes, and the formation constants are higher than about 10^8; thus SGCR is available as an indicator for these metal ions in alkaline media. However, it is not suitable for use with the other metals investigated here.

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