Reactions of Thiazolidine-2-thiones with Copper(II)

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A comparison of 3-alkyl-5-hydroxy-5-(1,2,3,4-tetrahydroxy-n-butyl)thiazolidine-2-thiones (Httt), which are sensitive, specific, spectrophotometric reagents for Cu^{II}, with more 'simple' thiazolidine-2-thiones shows that the Httt reagents differ from the latter in that no simple co-ordination compounds are formed with Cu^{II} ions. Instead, the Httt molecules undergo intramolecular rearrangements in the presence of Cu^{II} ions to afford dithiocarbamic acids which then readily bond to Cu^{II} as the dithiocarbamate anions. The products, $Cu(ttt)_2$, possess all the characteristics of the known copper dithiocarbamates. The specificity of Httt as analytical reagents for Cu^{II} is explained in terms of the inability of most other metal ions to induce the intramolecular rearrangement of Httt to form the dithiocarbamic acid.

3-ALKYL-5-HYDROXY-5-(1,2,3,4-TETRAHYDROXY-n-BUTYL)THIAZOLIDINE-2-THIONE derivatives [Httt, (I)] have been utilised as sensitive, specific, spectrophotometric reagents for copper(II) ions in solution.[1-3] The nature of the copper complexes formed by these reagents has not been fully established, however. Determination of the nature of the complexes formed with copper(II)

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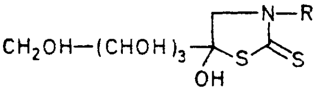
[1] J. A. Corbett, *Talanta*, 1966, **13**, 1089.

[2] M. J. Stiff, *Analyst*, 1972, **97**, 146.

[3] W. D. Basson and D. P. Venter, *Analyst*, in the press.

ions by the continuous variation and molar ratio methods gave ratios [1,2] of Cu : reagent of between 1 : 2 and 1 : 3 depending on the pH of the solution and the alkyl group of the ligand (I; R = Me,[1] Pr^n[2]).



Httt

(I)

The sensitivity of the various Httt reagents utilised for copper(II) determinations was found [3] to vary with R. The present study has indicated the benzyl derivative (Hbttt) to be the most sensitive reagent of the series [R = Me,[1] Pr^n,[2] Et, Pr^i, Bu^n, Bu^i, Bu^s,[3] Bz]. A detailed study of only the benzyl derivative was thus initiated and we report here the results of physical studies on the copper(II) complex formed as well as studies on more 'simple' thiazolidine-2-thione derivatives of copper.

Analytical, physical, and spectroscopic data

Compound	Colour	C	H	N	S	Conductivity/ Ω^{-1} cm^2 mol^{-1}	$\mu_{eff.}$/ B.M.	Charge-transfer band/nm	*d–d* Absorption band/nm
		(%, calculated values in parentheses)							
Hbttt	White	48·65 (48·68)	5·67 (5·54)	4·05 (4·05)	18·53 (18·86)				
$Cu(bttt)_2,H_2O$	Dark brown	43·51 (43·65)	4·81 (4·97)	3·69 (3·64)	16·85 (16·65)	0·5 [a]	1·77	429 [d]	618 [d] 628 [e]
$Cu(mbt)_2$	Yellow					1·2 [b]	0·77		975 [e]
$Cu(ttz)_2$	Yellow	24·14 (24·03)	2·77 (2·69)	9·96 (9·34)	43·17 (43·40)	0·8 [b]	0·79		1012 [e]
$Cu(Et_2NCS_2)_2$	Dark brown						1·67 [c]	432 [d]	618 [d] 632 [e]
$CuCl_2$ (anhydrous)							1·74		945 [e]

[a] 2×10^{-3}M Solution in acetone. [b] 1—10 $\times 10^{-4}$M Solutions in dimethyl sulphoxide. [c] $Cu(Pr^n_2NCS_2)_2$; L. Malatesta, *Gazetta*, 1940, **70**, 553. [d] Ethanol solution. [e] Dimethyl sulphoxide solution.

RESULTS AND DISCUSSION

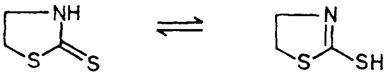
Reaction of 3-benzyl-5-hydroxy-5-(1,2,3,4-tetrahydroxy-n-butyl)thiazolidine-2-thione (Hbttt) with Cu^{II} ions in water–alcohol, alcohol, acetone, or dimethyl sulphoxide afforded a brown solution from which a dark brown precipitate could be obtained; no crystals of the product were isolated. Similar difficulties were also encountered when other of the Httt reagents were used. The brown precipitate is soluble in acetone, ethanol, and dimethyl sulphoxide, slightly soluble in water–alcohol, and insoluble in chloroform or dichloromethane and was shown from analytical results to have the stoicheiometry $Cu(bttt)_2,H_2O$. Conductivity measurements in acetone established the compound to be neutral, while an effective magnetic moment of 1·77 B.M. was obtained for the solid compound at room temperature. The electronic absorption spectrum of $Cu(bttt)_2,H_2O$ in the visible region contains peaks at 429 nm ($\varepsilon_{max.}$ 16 300, ethanol solution) and 618 nm (shoulder, broad, low intensity, ethanol solution).

The mode of bonding of the ttt ligands to the central Cu^{II} ion presented a problem; each ligand has to change to an anionic form before neutral Cu^{II} complexes can be obtained. Further, the ^1H n.m.r. ([$^2H_6$]dimethyl sulphoxide solution) and i.r. (KBr disc) spectra of $Cu(ttt)_2,xH_2O$ are complex and structural assignments could not be made from these.

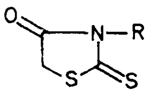
With a view to obtaining analogous type compounds possessing less complex spectroscopic characteristics, the reactions of Cu^{II} ions with benzo[*d*]thiazole-2-thione (Hmbt, IIb) and thiazolidine-2-thione (Httz, IIIa) in solution were investigated. This study, together with the data obtained from the literature, showed that thiazolidine-2-thiones react with Cu^{II} ions in solution by reducing Cu^{II} to Cu^I, and by forming two different classes of co-ordination compounds with Cu^{II}.

Rhodanine (IV; R = H) and its 3-methyl and 3-n-butyl derivatives are known [4] to reduce Cu^{II} to Cu^I and to co-ordinate to the Cu^I *via* the thiocarbonyl group of the ligand.

(IIa) Hmbt (IIb)



(IIIa) Httz (IIIb)



(IV)

Copper(II)–*Thiazolidine-2-thione Complexes which differ from* $Cu(ttt)_2,xH_2O$.—N.m.r. and i.r. data indicate that benzo[*d*]thiazole-2-thione exists entirely in the thioketo form (IIb) in solution but reacts with certain platinum metals by changing into the thiol

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[4] F. G. Moers and J. J. Steggerda, *J. Inorg. Nuclear Chem.*, 1968, **30**, 3217.

form.[5] The ring S and N heteroatoms as well as the mercaptide sulphur are capable of co-ordination to these metals.[5,6] The yellow Cu^{II} derivative, $Cu(mbt)_2$, which is only slightly soluble in acetone or ethanol, contains the mbt anion co-ordinated to the copper(II) ion *via* the N heteroatom and the mercaptide sulphur.[7-9] The electronic absorption spectrum of $Cu(mbt)_2$ contains a very broad peak of low intensity at 975 nm (DMSO solution) and the compound has a room temperature effective magnetic moment of 0·77 B.M.

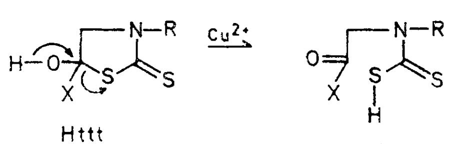
Reaction of copper(II) ions with thiazolidine-2-thione (ttz, IIIa) in ethanol–dimethyl sulphoxide afforded a yellow complex which is slightly soluble in acetone and alcohol. Analytical results showed the compound to have the stoicheiometry $Cu(ttz)_2$ while a conductivity measurement in dimethyl sulphoxide established it to be neutral. The room temperature effective magnetic moment of $Cu(ttz)_2$ is 0·79 B.M. The electronic absorption spectrum of this product contains a very broad peak of low intensity at 1012 nm (DMSO solution). It is proposed that thiazolidine-2-thione changes into the thiol form (IIIb) in solution and then bonds to Cu^{II} *via* the mercaptide sulphur and either the N or S heteroatom of the ligand although ttz has been postulated to be in the thioketo tautomeric form (IIIa) when bonded to the metals Co^{II}, Ni^{II}, Zn^{II}, Cd^{II}, and Hg^{II}.[10-12]

It is evident from the physical data that the copper–thiazolidine-2-thione complexes discussed above are simple co-ordination complexes involving copper(II) and the respective ligands. The anomalously low effective magnetic moments observed for $Cu(mbt)_2$ and $Cu(ttz)_2$ were not further investigated although similar anomalously low magnetic moments in some copper(II) complexes of Schiff bases derived from *S*-methyldithiocarbazate were interpreted in terms of antiferromagnetic interactions.[13]

$Cu(ttt)_2,xH_2O$ *Type Complexes*.—The most obvious difference between complexes of the type $Cu(ttt)_2,xH_2O$ and those formed by the reaction between Cu^{II} ions and the ligands mentioned above, *viz.* mbt and ttz, is in their colours and thus in their respective electronic absorption spectra; only the $Cu(ttt)_2,xH_2O$ type complexes possess a strong absorption band at *ca.* 430 nm. The broad, low intensity, absorption band at *ca.* 620 nm [$Cu(ttt)_2,xH_2O$ type complexes] is also shifted to *ca.* 975 nm for all other complexes under discussion.

Chemical studies have established that acetylation[14] of the 5-hydroxy group in Httt affords a ligand which reacts only very slowly with Cu^{II} in solution to form a complex of the type $Cu(ttt)_2$. Dehydration[14] of Httt removes the 5-hydroxy group and affords a ligand which does not form a complex of the type $Cu(ttt)_2$. Direct participation of the 5-hydroxy group in Httt on co-ordination to Cu^{II} was thus clearly demonstrated. Evidence that the Httt ligands are further involved in intramolecular rearrangements on co-ordination to Cu^{II} was obtained from i.r. studies; the i.r. spectrum of $Cu(bttt)_2,H_2O$ contains an absorption band in the C–O stretching frequency region (1735 cm^{-1}, KBr disc) while the i.r. spectrum of the ligand does not contain a corresponding peak.

A comparison of the physical properties of Cu^{II} dithiocarbamates, $Cu(R_2dtc)_2$, with those of $Cu(ttt)_2$ shows a remarkable similarity, *e.g.* the electronic absorption spectra of ethanol solutions of both compounds contain a peak of high intensity at *ca.* 430 nm as well as a very broad peak of low intensity at 618 nm. It is thus postulated that Httt undergoes an intramolecular rearrangement reaction in the presence of Cu^{II} ions to afford a dithiocarbamic acid (V) which then bonds to Cu^{II} as the dithiocarbamate anion. This would account for the neutral character of $Cu(ttt)_2,xH_2O$. The necessity of the presence of a 5-hydroxy group in Httt for the course of the intramolecular rearrangement reaction is understood in terms of the mechanism postulated in the Scheme.



Httt (V)

SCHEME

It was observed that this intramolecular rearrangement reaction was not induced by Fe^{II}, Co^{II}, Zn^{II}, Ag^{I}, MoO_2^{2+}, or UO_2^{2+} ions and only to some extent by Ni^{II} and Fe^{III} ions in solution although these metals are known to form dithiocarbamate complexes.[15] The rather unique ' catalytic ' intramolecular rearrangement effect Cu^{II} has on Httt readily explains the analytical specificity of Httt towards copper.

The electronic absorption spectrum of $Cu(ttt)_2,xH_2O$ is readily explained in terms of a charge-transfer transition ($L \longrightarrow M$) at 429 nm [$Cu(bttt)_2,H_2O$, ethanol solution] and a *d–d* transition at 618 nm [centre of broad peak, $Cu(bttt)_2,H_2O$, ethanol solution] (ref. 16). The i.r. spectrum of $Cu(bttt)_2,H_2O$, though complex, is not inconsistent with the presence of dithiocarbamate groups; absorption bands in the region attributed[17] to the $=N-\overset{|}{C}=S$ group can be identified (1485, 1355,

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[5] R. F. Wilson and P. Merchant, *J. Inorg. Nuclear Chem.*, 1967, **29**, 1993.

[6] V. M. Shulman, T. V. Zagorskaya, I. M. Cheremisina, G. K. Parygina, and E. A. Kravtsova, *Russ. J. Inorg. Chem.*, 1972, **17**, 1306.

[7] J. A. S. Cavaleiro and V. P. Crespo, *Rev. Port. Quim.*, 1970, **12**, 65.

[8] F. J. Welcher, ' Organic Analytical Reagents,' van Nostrand, New York, 1948, vol. 4, p. 109.

[9] E. J. Duff, M. N. Hughes, and K. J. Rutt, *J. Chem. Soc.* (*A*), 1968, 2354.

[10] P. P. Singh and R. Rivest, *Canad. J. Chem.*, 1968, **46**, 2361.

[11] D. De Filippo and C. Preti, *J. Chem. Soc.* (*A*), 1970, 1904.

[12] D. De Filippo, F. Devillanova, C. Preti, and G. Verani, *J. Chem. Soc.* (*A*), 1971, 1465.

[13] M. Akbar Ali, S. E. Livingstone, and D. J. Phillips, *Inorg. Chim. Acta*, 1973, **7**, 179.

[14] L. K. Dalton, *Austral. J. Chem.*, 1966, **19**, 445.

[15] D. Coucouvanis, *Progr. Inorg. Chem.*, 1970, **11**, 233.

[16] C. K. Jørgensen, *Inorg. Chim. Acta Rev.*, 1968, **2**, 65.

[17] A. T. Pilipenko and N. V. Melnikova, *Russ. J. Inorg. Chem.*, 1969, **14**, 236.

900 cm^{-1}, KBr disc). The water molecule in Cu(bttt)$_2$,H$_2$O is also readily identified. A comparison of the position of the *N*-methyl proton resonances in the n.m.r. spectra of Cu(I; R = Me)$_2$,xH$_2$O and (I; R = Me) respectively further clearly indicates that the N atom is not involved in the bonding between ttt and the Cu^{II} ion; the position of the *N*-methyl proton resonance is unchanged on complex formation. The presence of a water molecule in Cu(bttt)$_2$,H$_2$O is again verified from the n.m.r. spectrum.

The structure of Cu(ttt)$_2$ in solution is expected to be similar to the known Cu(R$_2$dtc)$_2$ derivatives, *viz.* square planar Cu^{II} environment.[15] The crystal structure of Cu(R$_2$dtc)$_2$ revealed the existence of lateral centrosymmetric dimers in which each copper ion adopts a square pyramidal co-ordination sphere.[15] Whether the carbonyl group of the bonded ttt-dithiocarbamate ligand in solid Cu(ttt)$_2$ is involved in intermolecular bonding to copper cannot be deduced from the data obtained so far. A molecular model of Cu(ttt)$_2$ does, however, indicate that the carbonyl group is unlikely to be involved in intramolecular bonding to the copper(II) ion.

EXPERIMENTAL

The ligands (I; R = Bz, Me) as well as the acetylated and dehydrated forms of (I; R = Bz) were synthesized according to the methods of Dalton.[14] Benzo[*d*]thiazole-2-thione and thiazolidine-2-thione were obtained commercially (Merck). The electronic absorption, i.r., and n.m.r. spectra were recorded on Cary 14, Beckman IR 12, and Varian HA 100D instruments, respectively. Conductivities were determined using a Metrohm E365B conductoscope. The elemental analyses were performed by Mr. G. J. Roberts, National Chemical Research Laboratory, C.S.I.R., Pretoria. The magnetic susceptibilities were measured by the Gouy method on a Newport Instruments single-temperature Gouy balance.

Bis[N-*benzyl*-N-(2-*oxo*-3,4,5,6-*tetrahydroxyhexyl*)*dithiocarbamato*]*copper*(II) *Monohydrate*, Cu(bttt)$_2$,H$_2$O.—Cu(NO$_3$)$_2$,3H$_2$O (0·19 g; 0·79 mmol) was dissolved in water (*ca.* 10 cm^3) and added dropwise to a stirred solution of 3-benzyl-5-hydroxy-5-(1,2,3,4-tetrahydroxy-n-butyl)thiazolidine-2-thione (0·06 g; 1·74 mmol) in ethanol (*ca.* 100 cm^3). The reaction mixture was stirred for 10 min and then concentrated to a smaller volume and allowed to stand. A brown precipitate separated from the solution over a period of 12 h. The mother liquor was decanted off and the precipitate washed with ethanol–water (yield, 60%).

Bis(*thiazolidine*-2-*thionato*)*copper*(II), Cu(ttz)$_2$.—Cu(NO$_3$)$_2$,3H$_2$O (0·66 g; 2·7 mmol) was dissolved in ethanol (*ca.* 100 cm^3) and added dropwise to a stirred solution of thiazolidine-2-thione (0·71 g; 6·0 mmol) in a mixture of ethanol (*ca.* 200 cm^3) and dimethyl sulphoxide (*ca.* 30 cm^3). The reaction mixture was stirred for 20 min, filtered, and then concentrated to a smaller volume and allowed to stand. A yellow precipitate separated from the solution. The mother liquor was decanted off and the precipitate washed with water and acetone (yield, 50%).

Cu(mbt)$_2$ [7-9] and Cu(Et$_2$NCS$_2$)$_2$ [15] were prepared by methods similar to those given above with a ratio of Cu : ligand of 1 : 2·2.

[3/2554 *Received*, 17*th December*, 1973]