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Sulphur–Nitrogen Chelating Agents.
Part I. Some Copper(II) Complexes of Sulphur-containing α,ω-Diamines

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Some series of five- and six-coordinated complexes of general formulae $Cu\{R_2N(CH_2)_nS(CH_2)_mNH_2\}X_2$ *or* $Cu\{R_2N(CH_2)_nS(CH_2)_mNH_2\}ZY$ *(n, m = 2 or 3; R =* CH_3 *or H; X =* NO_3^-, Cl^-, Br^-, ClO_4^-; *Z =* OAc^-, NO_3^-; *Y =* ClO_4^-, OH^-*) have been prepared and characterized. Structure assignment of the complexes is based on their conductivities in methanol, on their I.R. and electronic spectra. Dependent on the anion the n,m-*R_2*NSN ligand may be facially or meridionally disposed around the central Cu(II) ion. The parallelism between the electronic spectra of the solid* $\{Cu(n,m\text{-}R_2NSN)OAc\}ClO_4$ *complexes and the electronic spectra of the corresponding* $\{Cu(n,m\text{-}R_2NSN)3H_2O\}^{2+}$ *species in aqueous solution suggests structural similarity.*

Introduction

We recently have studied** the complexation in aqueous solution of the copper(II) ion with some α,ω-thiadiamines of the type $R_2N(CH_2)_nS(CH_2)_mNH_2$ (R = H, CH_3; n, m = 2, 3) [1]. In order to obtain more structural information we now have extended this investigation to a spectroscopic study of a series of solid $CuLX_2$ complexes (L = α,ω-thiadiamine; X = NO_3^-, OAc^-, ClO_4^-, Cl^-, Br^-, OH^-). The ligands studied together with the physical properties and analytical data of their complexes are given in Table I.

Some solid Cu(II) complexes with tridentate ligands containing a central sulphur donor and anions of differing coordinating ability have already been studied [2]. It has been shown that in most cases the metal ion was facially surrounded by the ligand with the sulphur donor bound in an axial position.

Results and Discussion

The most important I.R. bands are summarized in Tables II and III. Data of the electronic reflectance spectra or of the electronic absorption spectra in aqueous solution are listed in Table IV. It may be seen from Table II that for all complexes the N–H stretchings occur at appreciably lower frequencies than in the case of the free α,ω-thiadiamines. This may be considered as evidence for coordinated CH_3-NH or NH_2 groups [3]. Nevertheless, lowering of the N–H frequencies must also be attributed to hydrogen bonding between the anion and the ligand [4]. Indeed, N–H shifts are always the smallest for the perchlorate complexes, in agreement with the low proton acceptor strength of this ion [5]. However, the ability of the ligands to act as tridentates towards Cu(II) has already been shown [1].

Complexes of the Type $\{Cu(n,m\text{-}R_2NSN)X_2\cdot H_2O\}$ *(*$X^- = NO_3^-$ *or* ClO_4^-*)*

The hydrates $\{Cu(2,2\text{-}(Me)NSN)(NO_3)H_2O\}NO_3$ and $\{Cu(2,3\text{-}NSN(NO_3)\cdot H_2O\}NO_3$ were stable even at 110 °C, which suggests coordinated water molecules. The coordination mode of the nitrate group in these species may be obtained from their I.R. data [6–8]. From Table III it may be seen that $\{Cu(2,3\text{-}NSN)(NO_3)\cdot H_2O\}NO_3$ contains an ionic {bands at 825 cm^{-1}, 1350–1320 cm^{-1} and a single band at 1750 cm^{-1}} and a bidentate {bands at 808 cm^{-1}, 1500 cm^{-1} and at 1762, 1730 cm^{-1} (Δ = 32 cm^{-1})} nitrate group. For $\{Cu(2,2\text{-}(Me)NSN)(NO_3)\cdot H_2O\}NO_3$ it is more likely to accept an ionic {bands at 827 cm^{-1}, 1319 cm^{-1}, 1748 cm^{-1}} and a monodentate {bands at 821 cm^{-1} and 1758–1748 cm^{-1} (Δ = 10 cm^{-1})} nitrate group. The low values of $\Delta(\nu_1 + \nu_4)$ suggest a weak Cu(II) interaction, which can be realized with asymmetrically bound bidentate or axially disposed monodentate nitrate groups [7, 8]. We therefore accept for $\{Cu(2,2\text{-}(Me)NSN)(NO_3)\cdot H_2O\}NO_3$ a structure as given in Fig. 1a. Such a structure agrees also very well with the

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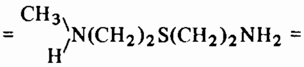
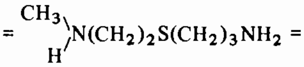
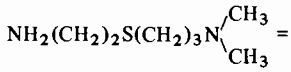
**For the abbreviations see also ref. 1.

TABLE I. Analysis, Colors and Molar Conductances of Some Cu(α,ω-thiadiamine)X_2 Complexes.

Complex	Found %				Calculated %				Color	Λ_m[a]
	Cu	N	C	H	Cu	N	C	H		
L = $NH_2(CH_2)_2S(CH_2)_2NH_2$ = 2,2-NSN										
$CuL(OH)(NO_3)$	24.3	16.00	18.35	4.94	24.17	16.03	18.27	4.95	blue grey	c
$CuL(OAc)(ClO_4)$[b]	18.7	–	–	–	18.55	–	–	–	blue	108
$CuL(ClO_4)_2 \cdot H_2O$	16.0	–	–	–	15.95	–	–	–	grey	c
$CuLBr_2$	18.68	8.01	13.71	3.29	18.48	8.16	13.98	3.49	olive green	d
$CuLCl_2$	24.75	10.86	18.9	4.62	24.93	10.99	18.84	4.71	dark green	d
L = $NH_2(CH_2)_2S(CH_2)_3NH_2$ = 2,3-NSN										
$CuL(NO_3)_2 \cdot H_2O$	18.82	16.30	17.47	–	18.69	16.48	17.66	–	grey	c
$CuL(OAc)(ClO_4)$	17.88	–	–	–	17.82	–	–	–	blue	97
$CuLBr_2$	17.78	7.79	16.84	3.79	17.76	7.83	16.78	3.91	blue	80
$CuLCl_2$	23.31	10.52	22.47	5.17	23.63	10.42	22.33	5.21	blue	83
L =  $(CH_3)(H)N(CH_2)_2S(CH_2)_2NH_2$ = 2,2-(Me)NSN										
$CuL(NO_3)_2 \cdot H_2O$	18.95	16.27	17.38	–	18.69	16.48	17.66	–	blue-purple	c
$CuL(OAc)(ClO_4)$	18.14	–	–	–	17.82	–	–	–	blue	99.1
$CuLBr_2$	17.83	7.87	16.75	3.72	17.76	7.83	16.78	3.91	olive green	d
$CuLCl_2$	24.29	10.51	22105	5.12	23.63	10.42	22.33	5.21	pale green	d
L =  $(CH_3)(H)N(CH_2)_2S(CH_2)_3NH_2$ = 2,3-(Me)NSN										
$CuL(OAc)(ClO_4)$	16.9	–	–	–	17.15	–	–	–	blue	96.9
$CuLBr_2$	16.99	7.49	19.24	4.16	17.09	7.53	19.38	4.31	green	81
$CuLCl_2$	22.67	9.80	25.12	–	22.48	9.91	25.49	–	green	74
L =  $NH_2(CH_2)_2S(CH_2)_3N(CH_3)_2$ = 2,3-NSN(Me_2)										
$CuLBr_2$	16.27	–	21.56	–	16.47	–	21.79	–	dark green	59
$CuLCl_2$	21.42	–	28.24	–	21.40	–	28.31	–	green	64

[a] Conductivities measured at 25 °C as 10^{-3} *M* solutions in methanol; Λ_m in ohm^{-1} cm^2 mol^{-1}. [b] C, N and H analysis not performed because of explosion danger by heating perchlorates. [c] Decomposes in methanol solution. [d] Not soluble in methanol.

TABLE II. The N–H Stretching Frequencies (cm^{-1}) in the Free Ligands and in Their Cu(II) Complexes.

Compound	ν_{N-H}			
	ν_{as}		ν_s	
2,2-NSN	3360m		3280m	
Cu(2,2-NSN)(OAc)(ClO_4)	3332m	3280m	3175m	
Cu(2,2-NSN)(OH)(NO_3)	3325m	3277m	3242s	3158m
Cu(2,2-NSN)$(ClO_4)_2 \cdot H_2O$	3330s	3278s	3220m	3172s
Cu(2,2-NSN)Br_2	3259m	3200m	3245m	3125m

(continued on facing page)

TABLE II. *(continued)*

Compound	ν_{N-H}		
	ν_{as}		ν_s
Cu(2,2-NSN)Cl_2	3275m 3208m		3245m 3138m
2,3-NSN	3365m		3285m
Cu(2,3-NSN)(OAc)(ClO_4)	3332s 3278s		3179w
Cu(2,3-NSN)$(NO_3)_2 \cdot H_2O$	3239w,br		3158w,br
Cu(2,3-NSN)Br_2	3290w 3245m		3185m 3119m
Cu(2,3-NSN)Cl_2	3300w 3275s		3195m 3125s
2,2-(Me)NSN	3360s,br		3280s,br
Cu(2,2-(Me)NSN)(OAc)(ClO_4)	3325s 3281s		3170w
Cu(2,2-(Me)NSN)$(NO_3)_2 \cdot H_2O$	3275m 3230m		3150m
Cu(2,2-(Me)NSN)Br_2	3265w 3213m		3123w
Cu(2,2-(Me)NSN)Cl_2	3270w 3220s		3138m
2,3-(Me)NSN	3360s		3285s
Cu(2,3-(Me)NSN)(OAc)(ClO_4)	3319m 3270m		3170w
Cu(2,3-(Me)NSN)Br_2	3276w 3230w	3190w	3170m 3115w
Cu(2,3-(Me)NSN)Cl_2	3310w 3250w	3199w	3158w 3137w
2,3-NSN(Me_2)	3365m		3290m
Cu{2,3-NSN(Me_2)}Br_2	3258w 3200w		3120w
Cu{2,3-NSN(Me_2)}Cl_2	3262s 3205m		3130m

s = strong, m = medium, w = weak, br = broad.

TABLE III. Characteristic IR Frequencies (cm^{-1}) of the Polyanions (NO_3^-), (OAc^-) and (ClO_4^-) in Cu(n,m-R_2NSN)X_2 Complexes.

Compound	NO_3^-			OAc^-			ClO_4^-	
	ν_2	ν_3	$(\nu_1 + \nu_4)$	ν_{as}(OCO)	ν_s(OCO)	Δ	ν_3	ν_4 (δ_{OClO})
L = 2,2-NSN								
CuL(OAc)(ClO_4)	–	–	–	1535s,sp	1415s,br	120	1100s,br	628s,sh
CuL(OH)(NO_3)[a]	822w	? , 1315m	1761vw 1740w	–			–	
	810w	? , 1272m	1748vw					
CuL$(ClO_4)_2 \cdot H_2O$[b]				–			1100s,br	627s,sp; 633sh
L = 2,3-NSN		–	–					
CuL(OAc)(ClO_4)	–	–	–	1542s,sp	1420m,br	122	1100vs,br	625m,sp
CuL$(NO_3)_2 \cdot H_2O$[c]	825w	1350–20s,br	1762vw 1750w	–			–	
	808w	1500s, ?	1730vw					
L = 2,2-(Me)NSN								
CuL(OAc)(ClO_4)	–	–	–	1538s	1419m	119	1100vs,br	623s,sp
CuL$(NO_3)_2 \cdot H_2O$[d]	827m	1319s,br	1748m,sp	–			–	
	821m	1422m,br; 1319s,br	1758w,sh					
L = 2,3-(Me)NSN								
CuL(OAc)(ClO_4)	–			1537s	1418m	119	1100s,br	621s,sp

[a] ν_{O-H}: 3548w; 3480w,br. [b] ν_{O-H}: 3600m,br. [c] ν_{O-H}: 3556m,sp; 3480m,br. [d] ν_{O-H}: 3550w,sp; 3460w,br. s = strong; m = medium; w = weak; sp = sharp; sh = shoulder; br = broad; v = very.

TABLE IV. Direct Reflectance and Absorption Spectra of the Cu(n,m-R_2NSN)X_2 Complexes.

Compounds	ν_{d-d} (kK)	
	D.R.	H_2O^a
L = 2,2-NSN		
CuL(OAc)(ClO_4)	14.95	
CuL(OH)(NO_3)	15.05	
CuL(ClO_4)$_2$·H_2O	17.50	
CuLBr_2	15.90	
CuLCl_2	16.05	
$(CuL3H_2O)^{2+}$	–	15.19
L = 2,3-NSN		
CuL(OAc)(ClO_4)	15.70	
CuL(NO_3)$_2$·H_2O	18.40	
CuLBr_2	14.95	
CuLCl_2	14.80	
$(CuL3H_2O)^{2+}$	–	15.93
L = 2,2-(Me)NSN		
CuL(OAc)(ClO_4)	15.15	
CuL(NO_3)$_2$·H_2O	17.60	
CuLBr_2	15.00	
CuLCl_2	15.20	
$(CuL3H_2O)^{2+}$	–	15.29
L = 2,3-(Me)NSN		
CuL(OAc)(ClO_4)	15.70	
CuLBr_2	13.40	
CuLCl_2	13.30	
$(CuL·3H_2O)^{2+}$	–	15.80

[a] See also ref. 14.

reflectance spectrum (17.6 kK), which is typical for a highly tetragonally distorted complex [9, 10]. For {Cu(2,3-NSN)(NO_3)·H_2O}NO_3 there are still two plausible structures dependent on a meridional or facial arrangement of the α,ω-thiadiamine (Fig. 1a,c). However, its reflectance spectrum again fits well into the class of almost square planar complexes [10]. So, the structure with the meridional ligand is more acceptable (Fig. 1a).

The reflectance spectrum of Cu(2,2-NSN)(ClO_4)$_2$·H_2O is also similar to that of the dinitrates. The I.R. spectrum of the former shows splitting of the antisymmetric bending mode of the perchlorate group (628, 633 cm^{-1}), indicating that at least one of ClO_4^- groups acts as a weakly bound monodentate [11]. Whether or not the water molecule in this complex is coordinated could not be stated. However, a structure with an equatorial (NSN)O configuration and two weakly bound axial perchlorate groups, as was also proposed for {Cu(2,2-NNN)(ClO_4)$_2$·H_2O} [9], is most probable.

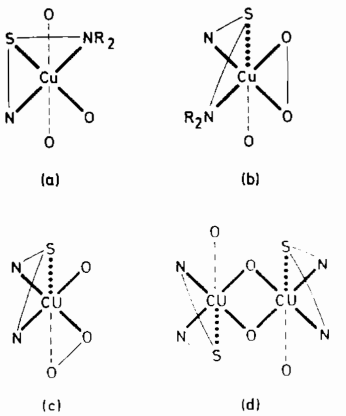


Fig. 1. Some possible structures for {Cu(n,m-R_2NSN)X_2·H_2O} and {Cu(n,m-R_2NSN)XY} complexes (X^- = NO_3^-, ClO_4^-; Z^- = OAc^-, OH^-, Y^- = ClO_4^-, NO_3^-).

{Cu(n,m-R_2NSN)XY} Compounds (Z^- = OAc^-, OH^-; Y^- = ClO_4^-, NO_3^-)

The d–d transitions of {Cu(n,m-R_2NSN)(OAc)}ClO_4 occur at much lower energy (14.95–15.7 kK) than for the {Cu(n,m-R_2NSN)X_2·H_2O} compounds (X^- = NO_3^-, ClO_4^-), which indicates that the former complexes are less tetragonally distorted. The separation (119–122 cm^{-1}) between ν_{as} and ν_s for the acetate group in their I.R. spectra (Table III) is much smaller than for {Cu(n,m-NNN)(OAc)}ClO_4 ($\Delta_{(\nu_{as}-\nu_s)}$ = 150–160 cm^{-1}), in which the acetate ion acts as an asymmetric bidentate [12]. It resembles closer the situation in {Zn(ethylenediamine)$_2$(OAc)}ClO_4 ($\Delta_{\nu_{as}-\nu_s}$ = 125 cm^{-1}), where the acetate group acts as a symmetric bidentate [12]. We therefore accept symmetrical bidentate coordination of the acetate group in our complexes, which implies a facial arrangement of the α,ω-thiadiamine. Furthermore the molar conductances indicate that the {Cu(n,m-R_2NSN)(OAc)}ClO_4 compounds are 1/1 electrolytes in methanol, which means that the perchlorate group is either ionically or only very weakly bound. All these arguments agree with an almost square pyramidal structure (Fig. 1,b).

As may be seen from Table IV, the d–d transition energies of the $\{Cu(n,m\text{-}R_2NSN)_3H_2O\}^{2+}$ species are almost the same as those for the corresponding {Cu(n,m-R_2NSN)(OAc)}ClO_4 complexes, having the same donor atoms (NSN, 3O). This means that also in aqueous solution the α,ω-thiadiamines are probably facially disposed in their 1:1 complexes, as was already expected [1].

The reflectance spectrum of {Cu(2,2-NSN)(OH)(NO_3)} is also very similar to that of {Cu(2,2-

NSN)(OAc)}ClO_4, assuming that the former also has the α,ω-thiadiamine facially disposed. The I.R. spectrum however is unique, since in spite of the presence of only one nitrate group, the spectrum gives evidence for a mono {822 cm^{-1}, 1315 cm^{-1} and 1741–1740 cm^{-1} (Δ = 8 cm^{-1})} and bidentate nitrate group. This means that the investigated sample contains a mixture of two closely related complexes. This may be explained by assuming monomeric complexes and dimeric complexes with bridging hydroxo-groups (Fig. 1c,d).

Cu(n,m-R_2NSN)Cl_2 and Cu(n,m-R_2NSN)Br_2 Complexes

For each individual α,ω-thiadiamine the I.R. spectra of its Cu(n,m-R_2NSN)Cl_2 and Cu(n,m-R_2-NSN)Br_2 complex are very similar in the region 4000–300 cm^{-1}, suggesting that both compounds are isostructural. In the region 300–200 cm^{-1} some mutual differences appear, which must probably be assigned to ν(Cu–Cl) and/or ν(Cu–Br) modes.

As may be seen from their solubility in methanol (Table I) our Cu(n,m-R_2NSN)X_2 complexes (X^- = Cl^- or Br^-) may be divided into two groups. First we have those complexes with the 2,2-NSN and 2,2-(Me)NSN ligands, which have equally-membered fused chelate rings and which are insoluble in methanol. They must be regarded as {Cu(2,2-R_2NSN)X_2} complexes. A second class, namely those with 2,3-R_2-NSN, show ring alternation and are almost 1/1 electrolytes in methanol. These complexes are therefore rather {Cu(2,3-R_2NSN)X}X complexes. However, since the bound halide donor in both types of complexes may bridge between two Copper(II) ions, dimeric compounds may not be excluded.

Experimental

Materials

The α,ω-thiadiamines were prepared by methods described elsewhere [1]. Copper(II) salts were commercially available except for $Cu(ClO_4)_2 \cdot 6H_2O$, which was obtained by treating {$CuCO_3 \cdot Cu(OH)_2$} with an excess $HClO_4$. The solid compounds Cu(n,m-R_2NSN)X_2 (X = Cl^-, Br^- or ClO_4^-) were prepared following the method of Taylor [2a]. The complexes Cu(2,2-NSN(OH)(NO_3) and Cu{2,2-(Me)-NSN}$(NO_3)_2 \cdot H_2O$ were obtained as follows. An ethanolic solution of 0.05 mol of the α,ω-thiadiamine was slowly added to an ethanolic solution of 0.05 mol $Cu(NO_3)_2 \cdot 3H_2O$ acidified with a very small amount of nitric acid. The complexes crystallized almost immediately. They were filtered off, washed with ethanol and ether and dried on P_2O_5 under reduced pressure. The preparation of Cu(2,3-NSN)$(NO_3)_2 \cdot H_2O$ in the same way failed. Nevertheless attempts to prepare Cu(2,3-NSN)(NO_3)(ClO_4) (see below) yielded only Cu(2,3-NSN)$(NO_3)_2H_2O$.

The compounds Cu(n,m-R_2NSN)(OAc)(ClO_4) were obtained by slowly adding 0.03 mol of the amine to an ethanolic solution of 0.015 mol $Cu(ClO_4)_2 \cdot 6H_2O$, 0.015 mol $Cu(OAc)_2 \cdot H_2O$ and a very small amount of acetic acid. The blue crystalline products precipitated within a minute. They were further treated as described for the nitrate compounds. Attempts to prepare Cu(n,m-R_2NSN)(NO_3)(ClO_4) following the same procedure failed.

Copper analyses were performed using an electrogravimetric technique [13]. A Coleman Model 33 and 29 analyzer was used to obtain the elemental C, H and N composition.

Electronic Spectra

Reflectance spectra in the region 12.8–28.0 kK were recorded with a Cary 14 spectrometer. The absorption spectra in solution were obtained as will be described in a following paper [14]. Reflectance spectra were recorded with $MgCO_3$ as reference.

I.R. Spectra

The I.R. spectra of the compounds were recorded as Nujol mulls on a Perkin-Elmer Model 580 double beam spectrophotometer in the region 4000–200 cm^{-1}. Since the ν_s(OCO) mode might be obscured by the broad nujol absorption near 1460 cm^{-1}, the I.R. spectra of the {Cu(n,m-R_2NSN)OAc}ClO_4 complexes were also obtained in PFC.

Conductivities

Molar conductances at 25 °C were measured on freshly prepared 10^{-3} *M* methanol solutions of the compounds with a Radiometer Conductivity Meter (type CDM 2^d) and a calibrated Radiometer Conductivity Cell (type CDC 104).

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References

1 a) G. G. Herman, A. M. Goeminne and Z. Eeckhaut, *J. Coord. Chem., 9,* 1 (1979).
b) G. G. Herman, A. M. Goeminne and H. F. de Brabander, *Thermochim. Acta, 32,* 27 (1979).
c) C. T. Huys, A. M. Goeminne and Z. Eeckhaut, *J. Inorg. Nucl. Chem.,* in press.
2 a) L. T. Taylor and E. K. Barefield, *J. Inorg. Nucl. Chem., 31,* 3831 (1969).
b) E. Uhlig, W. Hepp, Le My NGu and K. Schmiedeknecht, *Rev. Roumaine Chim., 22* (8) 1165 (1977).
3 F. A. Cotton, 'Modern Coordination Chemistry', Ed.

J. Lewis and R. G. Wilkins, Interscience, New York, ch. 5 (1960).

4 G. C. Pimentel and A. C. McClellan, 'The Hydrogen Bond', W. H. Freeman, London, 107 (1960).

5 L. J. Bellamy, 'The Infrared Spectra of Complex Molecules', Methuen, London (1958).

6 N. F. Curtis and Y. M. Curtis, *Inorg. Chem., 4,* 804 (1965).

7 A. B. P. Lever, E. Mantovani and B. J. Ramaswamy, *Can. J. Chem., 49,* 1957 (1971).

8 C. C. Addison, N. Logan, S. C. Walwork and C. D. Garner, *Quart. Rev., 25,* 289 (1971).

9 M. J. Bew, B. J. Hathaway and R. J. Fereday, *J. Chem. Soc. Dalton,* 1229 (1972).

10 B. J. Hathaway, *J. Chem. Soc. (A),* 1196 (1972).

11 B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.,* 3091 (1961).

12 N. F. Curtis, *J. Chem. Soc. (A),* 1579 (1968).

13 A. I. Vogel, 'A Textbook of Quantitative Inorganic Analysis', Longmans Green, London, 608 (1961).

14 C. T. Huys, G. G. Herman and A. M. Goeminne, to be published.