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Preparation and Properties of Cu(II) Complexes of *N*-Picolinoyl-*S*,*S*-tetramethylenesulfilimine, *N*-(Trimethylammonio)-picolinamidate, and Related Ylides

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The reactions of *N*-picolinoyl-*S*,*S*-tetramethylenesulfilimine (PS) and *N*-(trimethylammonio)picolinamidate (PA) with copper(II) chloride dihydrate in ethanol afforded complexes of the formula $CuCl_2(Y)$ and $CuCl_2(Y)_2$ (Y=PA or PS). The structures of these complexes were examined by spectroscopic and magnetic methods, and it was found that all of them have mononuclear chelate structures. It was concluded that in $CuCl_2(PS)$, the ligand is coordinated through two nitrogen atoms, whereas in $CuCl_2(PS)_2$, the ligands are coordinated through carbonyl oxygens and nitrogens in pyridine rings. The structures of $CuCl_2(PA)$, $CuCl_2(PA)_2$, and CuCl(PA) are closely similar to each other and the possibility of coordination through ylidic nitrogens with large ionic contributions to the structures was strongly suggested. Several Cu(II) complexes with monodentate sulfilimines and aminimides were also prepared, and the structural analyses revealed that the nature of the coordination depends largely on the structure of the ylides.

It has been reported that *N*-picolinoyl-*S*,*S*-tetramethylenesulfilimine (PS) and *N*-(trimethylammonio)-picolinamidate (PA) are bidentate and ambident ligands and form 1:1 chelate complexes with $PdCl_2$ and $PtCl_2$ in which the ligands are coordinated through two nitrogen atoms.[1)] In this paper the formation of Cu(II) and Cu(I) complexes of these ylides and the determination of their structure by magnetic and spectroscopic methods are reported. An interesting feature of the chemistry is the nature of the metal-ligand coordination bonds which has not been investigated in detail.

Although numerous reports have been published on the transition metal–ylide complexes, only a limited number of them describe copper complexes. Chia *et al.*[2)] claim that *N*-(1-pyridinio)benzenesulfonamidate forms complexes with Cu(II) perchlorate and halides *via* ylidic nitrogen atoms. Measurements of magnetic moments suggested a dimeric structure for the $CuCl_2$ complex, whereas *N*-(1-pyridinio)benzamidate gave a monomeric complex with $CuCl_2$ by coordination *via* ylidic nitrogen. Another Cu(II)–ylide complex reported is the reaction product of triphenylphosphonium phenacylide with $CuCl_2$,[3)] which is diamagnetic and likely to have a dimeric or polymeric structure.

Results and Discussion

Complexes of N-*Picolinoyl*-S,S-*tetramethylenesulfilimine (PS) with* $CuCl_2$. By addition of an ethanol solution of PS to an ethanol solution of $CuCl_2 \cdot 2H_2O$ in an equimolar ratio, a 1:1 complex was obtained as a precipitate. The magnetic moment of the complex (Table 1) is normal for an isolated Cu(II) metal and rules out dimeric or polymeric structures. The ylide PS has resonance structures shown below, and the anionic charge is considered to be delocalized over the N–C–O atoms. The large contribution of the enolate ion structure is confirmed by the low C=O stretching band (1547 cm^{-1}), which is comparable to that of carboxylate ions. The IR spectrum of the 1:1 complex exhibits a C=O stretching band at 1655 cm^{-1}, which is 108 cm^{-1} higher than that of the free ligand (Table 2) and close to the bands of carboxamides, clearly indicating coordination through ylidic nitrogen. The proposed square plannar structure in Fig. 1 (**1**) requires coordination through another nitrogen in the pyridine ring, and this is supported by the observed higher frequency shift of the pyridine deformation band from 615 cm^{-1} in the free ligand to 647 cm^{-1} in the complex.[4)] These results are quite similar to those of the complexes of PS with $PdCl_2$ and $PtCl_2$, and it may be concluded that the complex has a structure shown in Fig. 1 (**1**) in which the Cu(II)–ylidic nitrogen coordination is essentially covalent (σ) bonding. Although an alternative dimeric square plannar structure like that of dihalo(2-methylpyridine)copper(II) may be possible, in which the two planes interact through Cu–Cl–Cu bond,[5)] the inter-

Table 1. Analyses and properties of complexes

Complex	Yield (%)	Mp (°C)[a)]	Color	Found, % C	Found, % H	Found, % N	Calcd, % C	Calcd, % H	Calcd, % N	μ_{eff}[b)] (B.M.)
$CuCl_2(PS)$	84	>198	blue-green	34.25	3.40	8.70	35.04	3.54	8.18	1.96
$CuCl_2(PS)_2$	90	126—128	blue-green	43.98	4.97	9.96	43.59	4.40	10.17	1.86
$CuCl_2(FS)_2$	77	152—154	green-yellow	20.65	4.03	7.82	20.90	4.10	8.13	1.90
$CuCl_2(AS)$	43	127—128	red-brown	26.66	4.25	5.38	25.76	3.97	5.01	1.97
$CuCl_2(PA)$	79	215—216	blue	33.84	4.24	13.04	34.46	4.18	13.40	1.94
$CuCl_2(PA)_2$	96	192—193	blue	42.00	5.87	16.61	42.31	5.53	16.45	1.88
CuCl(PA)	75	195—196	blue-green	39.40	5.34	15.46	38.85	4.72	15.11	—
$CuCl_2(AA)$	87	190—191	yellow-brown	24.50	4.92	10.98	23.96	4.84	11.18	1.94
$CuCl_2(BA)$	75	122—125	red-brown	37.73	5.22	8.43	38.41	4.52	8.96	1.68

a) The complexes melt with decomposition. b) At room temperature.

Table 2. IR data of ylides and their complexes (cm^{-1})

Compound	C=O st.	Aromatic ring st.	C-N st.	Aromatic C-H def.	Pyridine def.
$(CH_2)_4S{=}NCOC_5H_4N$ (PS)	1547	1587	1330	750, 703	615
$CuCl_2$ (PS)	1655	1600	1320	760, 689	647
$CuCl_2(PS)_2$	1530	1606	1375	767, 691	656
$(CH_3)_2S{=}NCOH$ (FS)	1574	—	1233	—	—
$CuCl_2(FS)_2$	1600	—	1200	—	—
$(CH_2)_4S{=}NCOCH_3$ (AS)	1540	—	1290	—	—
$CuCl_2(AS)$	1502	—	1390	—	—
$(CH_3)_3\overset{+}{N}\text{-}\overset{-}{N}COC_5H_4N$ (PA)	1560	1605	1350	750, 705	623
$CuCl_2(PA)$	1585	1615	1360	758, 690	648
$CuCl_2(PA)_2$	1582	1610	1355	755, 690	655
$CuCl(PA)$	1582	1610	1355	755, 690	654
$(CH_3)_3\overset{+}{N}\text{-}\overset{-}{N}COCH_3(AA)$	1575	—	1335	—	—
$CuCl_2(AA)$	1570	—	1345	—	—
$(CH_3)_3\overset{+}{N}\text{-}\overset{-}{N}COC_6H_5$ (BA)	1560	1600	1334	726	—
$CuCl_2(BA)$	1690, 1545	1592	1352, 1275	710	—

action would be very weak considering the large magnetic moment of $CuCl_2(PS)$.

The electronic spectral data are summarized in Table 3. The ligand PS and PA have structural similarity to picolinamides which liberate a hydrogen atom in alkaline media to form neutral complexes with Cu(II). An example is shown in Fig. 1 (**7**) which was reported to be reddish violet and to have λ_{max} at 530 and 585 nm in chloroform and water, respectively.[6] It is interesting to note that in the case of $CuCl_2(PS)$, only a small difference in the absorption maximum was observed in chloroform and water, in contrast to complex **7** which shows a red shift in water due to the coordination of water to form an octahedral structure. The electric conductivity of $CuCl_2(PS)$ in chloroform is low and indicates no dissociation, but in water the complex is a strong electrolyte (Table 3). Therefore, the chloride ions are considered to be fully replaced by water, and this might compensate for the red shift which is expected in the change to the octahedral structure in water.

From the reaction of $CuCl_2\cdot 2H_2O$ with two equivalents of PS, a complex was obtained which was formulated as $CuCl_2(PS)_2$ and has the normal paramagnetic character of a monomeric structure. However, the C=O stretching absorption band appears at 1530 cm^{-1}, 17 cm^{-1} lower than that of the free ligand, in contrast to the higher frequency shift of $CuCl_2(PS)$ described above. In addition, the C–N stretching band shifts from 1330 to 1375 cm^{-1} indicating an increase in double bond character in the complex, and it is very likely that the ligands are coordinated through carbonyl oxygens.

Table 3. Electronic spectral data and molar conductivity of complexes

Complex	$\lambda_{max}(\varepsilon)$		Λ[a]	
	in H_2O	in $CHCl_3$	in H_2O	in $CHCl_3$
$CuCl_2(PS)$	715(27)	720(70)	267	1.03
$CuCl_2(PS)_2$	670(39)	820(106)	221	1.89
$CuCl_2(FS)_2$	815(15)	—[b]	274	—[b]
$CuCl_2(AS)$	800(13)	—[b]	202	—[b]
$CuCl_2(PA)$	710(24)	730(99)	250	1.04
$CuCl_2(PA)_2$	660(44)	850(155)	227	2.99
$CuCl(PA)$	660(41)	840(82)	117	1.72
$CuCl_2(AA)$	830(3.4)	—[b]	184	—[b]
$CuCl_2(BA)$	820(9.7)	—[b]	265	—[b]

a) Measured at 10^{-3} M, $\mho\ cm^2\ mol^{-1}$. b) Insoluble in $CHCl_3$.

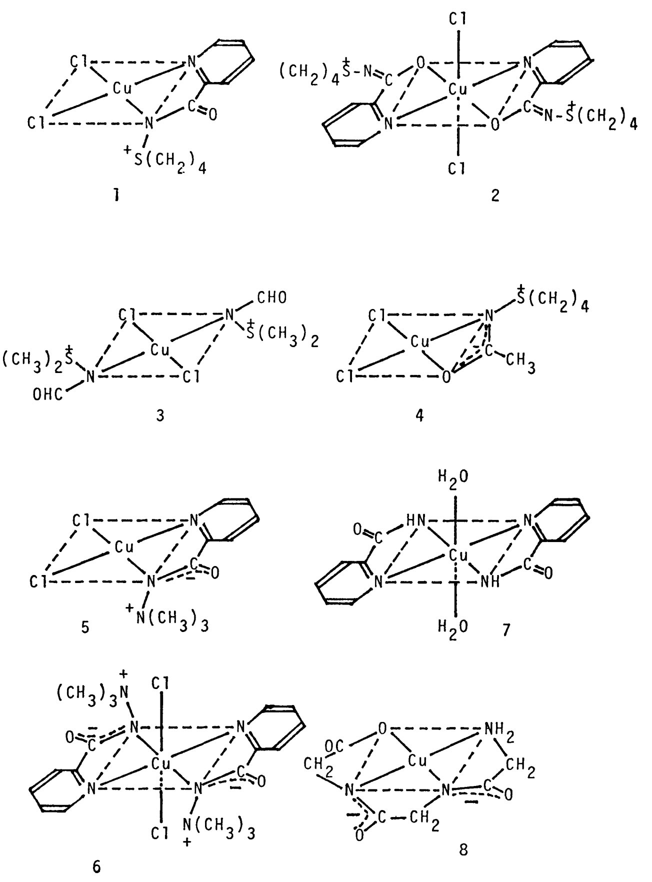
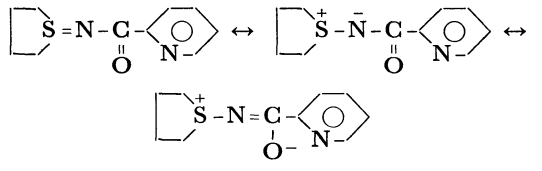
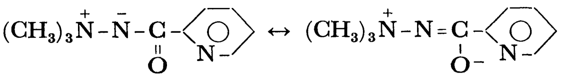


Fig. 1. Structure of Cu(II) complexes.

Although a large number of metal complexes of carbonyl-stabilized ylides have been reported, very few have coordination *via* carbonyl oxygens.[7] The change of the coordination site from the ylidic nitrogen to the carbonyl oxygen in going from 1:1 to 1:2 complexes may be the consequence of the steric hindrance around Cu(II). A close interaction observed in a structural model between a pyridine ring of a ligand and a tetramethylenesulfonium group in another one supports this consideration. The 1:2 complex is also a nonelectrolyte and has absorption maximum at 820 nm in chloroform, and an octahedral structure was proposed as shown in Fig. 1 (**2**). In water this complex is a strong electrolyte and the absorption band falls to 670 nm, probably because of the lowering of the microsymmetry to a more distorted octahedral or square plannar structure due to the weaker metal–chloride bonding by strong hydration of the chloride ions.



PS



PA

Complexes of N-*Formyl*-S,S-*dimethylsulfilimine (FS) and* N-*Acetyl*-S,S-*tetramethylenesulfilimine (AS) with $CuCl_2$.* These ligands behave quite differently in the complex formation. Elemental analyses reveal that the ylide FS forms a 1:2 complex, while AS forms a 1:1 complex. Furthermore, the former exhibits a C=O stretching band at 1600 cm^{-1}, 26 cm^{-1} higher than in the free ligand, whereas the latter exhibits the C=O band at 1502 cm^{-1}, 38 cm^{-1} lower than in the free ligand. Thus, metal–ylidic nitrogen and metal–carbonyl oxygen coordinations are implied for $CuCl_2(FS)_2$ and $CuCl_2(AS)$, respectively, and supported also by each observed shift of the C–N stretching band in going from the free ligands to the complexes. The complexes show normal paramagnetism (Table 1), and the most probable structures are indicated in Fig. 1 (**3**) and (**4**). Taking into consideration the small shift of the carbonyl band in $CuCl_2(FS)_2$, the Cu(II)–ylide bond is likely to have ionic character; that is, the ligand has appreciable ylidic nature retained in the complex. The structure in Fig. 1 (**4**) is similar to those of π-allyl complexes, but only few ylides have been reported to form complexes of this η^3 structure.[7] Electronic spectra were not obtained in nonpolar solvents because of the low solubility of the complexes, and the data available do not allow more positive conclusions on the structure of these complexes.

Complexes of N-*(Trimethylammonio)picolinamidate (PA) with $CuCl_2$ and CuCl.* Both 1:1 and 1:2 complexes of PA with $CuCl_2$ were prepared in similar ways to those of the PS complexes. In addition, the reaction of PA with two equivalents of CuCl afforded a 1:1 complex, CuCl(PA). A characteristic feature for these PA complexes is that they give almost identical IR spectra (Table 2), implying an identical coordination mode of the ligand in these complexes. The C=O bands appear near 1580 cm^{-1}, about 20 cm^{-1} higher than that of the free PA suggesting coordination *via* ylidic nitrogen. However, the shifts are relatively small compared to that observed in $CuCl_2(PS)$ and the complexes of PA with Pd(II) and Pt(II),[1] and the frequencies are much lower than that of picolinamide. The C=O band frequency of Pd(II) and Pt(II) complexes is sensitive to the structure of the ylide and has been discussed in terms of the covalent and ionic character of the metal–ylide bond.[1] Since the basicity of aminimides is higher than that of the sulfilimines,[8] the small frequency shifts of PA complexes are more likely to be a consequence of the large ionic character of the coordination than that of the weak covalent bond between Cu(II) and the ylides. The situation may be analogous to the Cu(II) complexes of oligopeptides, one of which is shown in Fig. 1 (**8**).[9]

The d-d transition spectra of $CuCl_2(PA)$ and $CuCl_2(PA)_2$ and their solvent effects are quite similar to those of $CuCl_2(PS)$ and $CuCl_2(PS)_2$ (Table 3), and analogous discussion may be made for the PA complexes and the proposed structures are shown in Fig. 1 (**5**) and (**6**).

The electronic spectrum and electric conductivity of CuCl(PA) as well as IR spectrum are close to those of $CuCl_2(PA)_2$. Therefore, the nature of the ligand coordination is considered to be similar to the Cu(II) complex, though it is difficult to draw any definite structure.

Complexes of N-*(Trimethylammonio)acetamidate (AA) and* N-*(Trimethylammonio)benzamidate (BA) with $CuCl_2$.* Both AA and BA afforded 1:1 complexes with $CuCl_2$, but the magnetic moment of the latter is lower than the supposed value for a monomeric structure, whereas the former gave a normal value for paramagnetism. In the case of $CuCl_2(AA)$, spectroscopic data are in accord with the structure analogous to **4** in Fig. 1, in which the ligand is coordinated through N and O atoms. On the other hand, the IR spectrum of BA complex exhibits two carbonyl absorption bands at 1545 and 1690 cm^{-1}. Considering also a low magnetic moment, the complex is considered to be a mixture of N- and O- bonded monomeric or polymeric structures.

Experimental

Melting points, uncorrected, were determined on a Yamato model MP-21 apparatus using open capillaries. Infrared spectra were taken on a JASCO IRA-2 spectrometer using KBr disks, and electronic spectra were recorded on a Union 401 spectrometer. Elemental analyses were performed on a Perkin Elmer 240 analyzer, and magnetic susceptibility was measured by the Faraday method at room temperature with a Shimadzu magnetic balance. Electric conductivity was determined with a Toa CM-2A conductometer at 25±0.2 °C.

The syntheses of the sulfilimines and aminimides which were used as ligands have been described in previous papers.[1,8]

Preparation of Complexes. The preparation of dichloro(*N*-picolinoyl-*S*,*S*-tetramethylenesulfilimine)copper(II), $CuCl_2(PS)$, is described as a standard method for the preparation of the complexes. A solution of *N*-picolinoyl-*S*,*S*-tetramethylenesulfilimine (PS) (0.456 g, 2.19 mmol) in ethanol (5 ml) was added with stirring to a solution of copper dichloride dihydtate (0.364 g, 2.14 mmol) in ethanol (5 ml) at room temperature. The mixture was stirred overnight, and the blue-green precipitate was separated by filtration, washed with small portions of ethanol and dried *in vacuo*. The product is soluble in water and methanol, slightly soluble in ethanol and chloroform, and insoluble in hydrocarbons. It gradually decomposes above 198 °C changing to a brown color. Reprecipitation from methanol-ether afforded the compound with almost the same spectroscopic properties and thermal stability as the crude product.

From the reaction of $CuCl_2 \cdot 2H_2O$ with two equivalents of the sulfilimine, a clear blue solution with a small amount of precipitate was obtained under the same conditions as described above. After the removal of the precipitates by filtration, ether was added to the filtrate and the precipitates formed were separated, washed with ether, and dried *in vacuo*. The product has the formula of $CuCl_2(PS)_2$ and is soluble in water and ethanol, partly soluble in chloroform, and insoluble in hydrocarbons.

Other complexes were prepared under essentially the same conditions as shown above, and the complexes $CuCl_2(FS)_2$, $CuCl_2(AS)$, $CuCl_2(PA)$, and $CuCl_2(AA)$ were obtained simply from the reaction mixture as precipitates, while $CuCl_2(PA)_2$, CuCl(PA), and $CuCl_2(BA)$ were obtained by the addition of ether to the reaction mixtures. The reactions of PS and AA with CuCl gave crude products which were not analytically pure and the purification was unsuccessful. The reaction of *N*-benzoyl-*S*,*S*-tetramethylenesulfilimine with $CuCl_2 \cdot 2H_2O$, and those of FS, AS, and BA with CuCl were also attempted, but no solid products were isolated by the above described methods.

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