DONOR-ACCEPTOR COMPLEXES

OF HETEROAROMATIC N-OXIDES

WITH COPPER AND ZINC CHLORIDES

V. P. Andreev, Ya. P. Nizhnik, S. G. Tunina, and B. Z. Belashev

Thirteen new molecular complexes of pyridine and quinoline N-oxides with CuCl₂ and ZnCl₂ of composition 1:1 and 2:1 have been obtained and characterized. Their structure depends on the constitution of the ligand, the nature of the metal, and the reactant ratio at complex formation.

Keywords: heteroaromatic N-oxides, donor-acceptor complexes, pyridine, quinoline, copper and zinc chlorides.

The present work is a continuation of investigations of the structure and properties of donor-acceptor complexes of the N-oxides of pyridines, quinolines, isoquinoline, and acridine with ν-acceptors. We showed previously that coordination in the above compounds is usually brought about at the oxygen atom of the N→O group with the formation of stable complexes of composition 1:1. The exception were adducts of 4-nitroquinoline with BF_3 (the donor centers are the oxygen atoms of the nitro group [1]), with HCl, HBr, and $AlCl_3$ (substitution of the nitro group by a halogen atom occurs rapidly [2]), and also complexes of the N-oxides of 4-(4-dimethylaminostyryl)quinoline and pyridine, in which second molecule of BF_3 or proton is readily added to the amino group [3].

Since the acceptors mentioned above are hard acids according to the Pearson principle, it seemed of interest to us to study complex formation with Zn^{2+} (borderline acid) and Cu^{2+} (soft acid) [4], all the more as the halides of these metals are frequently used in organic synthesis.

According to [5-7] N-oxides of pyridine and quinoline form adducts with zinc and copper salts, the structure of which depends on the type of anion. Zinc perchlorate or nitrate form crystals of composition ZnL_6X_2 (where L is N-oxide, X the anion), but the more basic chloride ion gives the ZnL_2X_2-type complex. With copper perchlorate adducts CuL_6X_2 and CuL_4X_2 are obtained, but with chloride and bromide – CuL_2X_2 and $CuLX_2$. In addition it was noted in [6] that the composition of complexes with $CuCl_2$ and $CuBr_2$ depends on the basicity of the ligand. The authors successfully obtained only complex of composition 1:1 for N-oxide of quinoline and its 6-methyl and 4-methyl derivatives, but for the less basic nitro and chloro derivatives the ligand–CuX_2 ratio was 2:3, 2:1, 1:1, or 3:4.

However the literature data are fragmentary and do not give a clear picture of the reasons for the existence of one or another type of complex. Consequently we attempted to assess the effect of different factors, particularly polar and steric effects, on the coordination process. Subjects selected for the investigation were, on the one hand, zinc and copper chlorides forming with pyridine N-oxides compounds of simpler structure than

salts with anions of lower basicity [5], and on the other hand N-oxides **1-3** without electron-withdrawing substituents reducing the basicity of the ligand, but with various steric environments about the N→O group, which usually participates in complex formation.
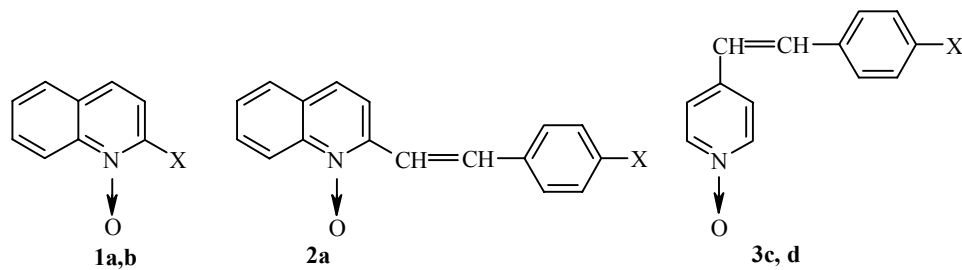
a X = H, **b** X = Me, **c** X = OMe, **d** X = NMe$_2$

The complexes of N-oxides **1-3** were isolated by us in the pure state from the appropriate saturated ethanol solutions of a mixture of donor and acceptor (Table 1).

It was discovered that with ZnCl$_2$ N-oxides **1a,b**, **2a**, and **3c** form only complexes with a ligand–ZnCl$_2$ ratio of 2:1, but N-oxide **3d** formed 1:1 complex as well. In the case of CuCl$_2$, also depending on the reactant ratio, adducts of composition 2:1 and 1:1 were formed. The exceptions were N-oxides **2a** and **3c** which form only 2:1 or 1:1 complexes respectively. We also recorded the existence of other types of adducts which were not isolated in pure state. After mixing N-oxides **1a,b** and **2a** with CuCl$_2$ a yellow solid precipitated, which in the course of several minutes, depending on the experimental conditions, was converted into complexes of composition 2:1 or 1:1. On mixing solutions of N-oxide **3c** and ZnCl$_2$ a small quantity of colorless crystals was

TABLE 1. Characteristics of Molecular Complexes of Heteroaromatic N-Oxides with CuCl$_2$ and ZnCl$_2$

N-Oxide (D)	MeCl$_2$ (A)	D:A	Color	mp, °C	Yield, %
1a	ZnCl$_2$	2:1	White	198-200	72
	CuCl$_2$	1:1*	Black-brown	208-209	58
	CuCl$_2$	2:1	Red	175-177	74
1b	ZnCl$_2$	2:1	White	220	60
	CuCl$_2$	1:1	Red-brown	166-167	61
	CuCl$_2$	2:1	Greenish brown	132	60
2a	ZnCl$_2$	2:1	Grayish yellow	222-223	70
	CuCl$_2$	2:1	Brown	186-187	72
3c	ZnCl$_2$	2:1	Yellow-orange	213-215	74
	CuCl$_2$	1:1	Black-brown	218-219	80
3d	ZnCl$_2$	2:1	Bright red	230-232	32
	ZnCl$_2$	1:1	Orange-red	225-235	76
	CuCl$_2$	1:1*2	Brown	—	75
	CuCl$_2$	2:1	Black-brown	145 (dec.)	60

_____

* The complex was synthesized previously [6], but its characteristics were not given.

*^{2} Melting point was not determined (no sharp visible changes in the state of the substance occurred).

precipitated initially, which with time gave a complex of composition 2:1. It should be mentioned that compound **3c** is yellow. It was shown previously in [3] that a similar hypsochromic effect on interaction of styryl derivatives of N-oxides with HCl and BF$_3$ was observed in those cases when the N→O group and OCH$_3$ [or N(CH$_3$)$_2$], which are in direct resonance conjugation with one another, participated simultaneously. This is related to a weakening of the processes of intramolecular charge transfer. Consequently it may be assumed that in the present case a complex of composition 1:2 is initially formed in the reaction mixture with ZnCl$_2$, which is gradually rearranged into the more stable 2:1 complex.

Data of electronic and IR spectroscopy enable all the isolated compounds to be assigned to complexes of the *n*,ν-type.

In the IR spectra of N-oxides **1-3** there are very strong bands for stretching vibrations characteristic of the N→O group at 1250-1365 cm^{-1} (Table 2). However in the spectra of their complexes with ZnCl$_2$ and CuCl$_2$ these bands are reduced in intensity or disappear altogether (adducts with N-oxide **3d**), and new bands appear at 1175-1210 cm^{-1} due to the formation of a donor–acceptor oxygen–metal bond, which is in agreement with the data for pyridine N-oxide [5]. In addition absorption bands arise at 300-350 cm^{-1} caused by the presence of a metal–chlorine bond [6].

In the electronic spectra of complexes of N-oxides **1a,b** and **2a** with ZnCl$_2$ and CuCl$_2$ of composition 2:1 (Table 3) in ethanol, chloroform, and methylene chloride the position of the long-wave absorption band is practically unchanged, but a significant hyperchromic effect is observed which may be caused by an increase in the length of the conjugation chain in the structure of compound **6** compared with the initial heteroaromatic compounds.
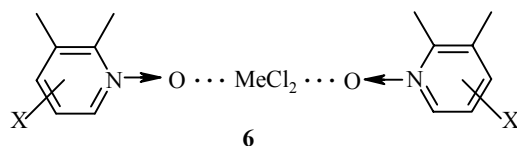
$$N \rightarrow O \cdots MeCl_2 \cdots O \leftarrow N$$

6

TABLE 2. Data of IR Spectroscopy in KBr of Heteroaromatic N-Oxides (D) and Their Molecular Complexes with ZnCl$_2$ and CuCl$_2$ (A)

N-Oxide	MeCl$_2$	D:A	Regions of bond vibrations (ν, cm^{-1})					
			N=O ↔ N$^+$–O$^-$			Me–Cl		
1a	—	—	1310 s	1267 s	—	—	—	
	ZnCl$_2$	2:1	1310 vw	1270 m	1177 m			307 s
	CuCl$_2$	1:1	1310 w	1272 m	1175 m	343 s	336 s	
	CuCl$_2$	2:1	1313 w	1270 m	1180 vs	350 w		320 m
1b	—	—	1340 vs	1272 m	—	—		
	ZnCl$_2$	2:1	1350 s	1275 w	1188 vs		328 m	305 s
	CuCl$_2$	1:1	1350 w	1277 vw	1186 m	340 s		310 s
	CuCl$_2$	2:1	1350 m	1278 w	1187 s	353 m	335 s	305 s
2a	—	—	1363 vs	1277 m	—	—		
	ZnCl$_2$	2:1	1358 m	1281 w	1206 s			
	CuCl$_2$	2:1	1363 w	1285 vw	1208 s	340 s	330 m	313 s
3s	—	—		1250 vs	—	—		
	ZnCl$_2$	2:1		1250 s	1210		325 w	310 w
	CuCl$_2$	1:1		1255 s	1205 m		325 w	300 w
3d	—	—		1260 vs	—	—		
	ZnCl$_2$	2:1		—	1207 s		325 w	310 w
	ZnCl$_2$	1:1		—	1207 s		330 m	311 w
	CuCl$_2$	1:1		—	1210 br		320 w	
	CuCl$_2$	2:1		—	1207 s		323 w	

TABLE 3. Electronic Spectra of N-Oxides (D) and Their Complexes with ZnCl$_2$ and CuCl$_2$ (A)

N-Oxide	MeCl$_2$	D:A	Solvent*	λ_{max}, nm (log ε)
1	2	3	4	5
1a	—	—	96% ethanol	210 sh; 231 (4.60); 325 (3.84); 340 sh (3.79)
			Chloroform	250 sh; 325 (3.82); 335 (3.89); 350 sh (3.83)
			CH$_2$Cl$_2$	247 (4.03); 327 sh (3.77); 339 (3.80); 355 sh (3.69)
	ZnCl$_2$	2:1	96% ethanol	207 (4.26); 231 (5.08); 318 sh (4.13); 326 (4.14); 340 sh (4.08)
			Chloroform	247 (4.57); 324 (4.28); 336 (4.33); 350 (4.22)
			CH$_2$Cl$_2$	242 sh (3.93); 245 (3.94); 250 sh; 270 sh; 313 sh; 322 (3.88); 335 (3.88)
	CuCl$_2$	1:1	96% ethanol	207 (4.06); 231 (4.87); 318 sh (3.88); 326 (3.89); 340 sh (3.82)
			CH$_2$Cl$_2$	250 sh (3.34); 326 (3.15); 340 (3.17); 354 (3.11); 379 (2.83)
	CuCl$_2$	2:1	96% ethanol	207 (4.02); 230 (4.57); 320 (3.83); 338 (3.80)
			CH$_2$Cl$_2$	250 sh (4.34); 326 (4.06); 339 (4.08); 354 (4.03); 380 (3.55)
1b	—	—	96% ethanol	213 sh; 230 sh; 237(4.60); 319(3.79); 328 sh
			Chloroform	310 (3.81); 321 (3.85); 343 sh (3.13)
			CH$_2$Cl$_2$	245 (4.36); 326 sh (3.51); 335 (3.85); 345 sh (3.47)
	ZnCl$_2$	2:1	96% ethanol	208 (4.40); 230 (4.88); 236 (4.94); 316 (4.15); 327 (4.09)
			Chloroform	246 (4.59); 327 (4.14); 342 sh (4.08)
			CH$_2$Cl$_2$	248 (4.23); 314 (4.24); 326 (4.22)
	CuCl$_2$	1:1	96% ethanol	208 (4.23); 230 sh (4.54); 236 (4.58); 310 (3.84); 331 sh (3.71); 368 sh
			CH$_2$Cl$_2$	250 sh (3.72); 313 (3.56); 318 (3.57); 323 (3.56); 347 (3.35); 385 (3.20)
	CuCl$_2$	2:1	96% ethanol	230 (4.95); 236 (5.01); 316 (4.19); 328 (4.14)
			CH$_2$Cl$_2$	250 sh (4.34); 326 (4.06); 339 (4.08); 354 (4.03); 380 (3.55)
2a	—	—	96% ethanol	202 (4.26); 208 sh; 237 (4.23); 247 sh; 300 (4.54); 308 (4.55); 350 sh (4.35); 360 (4.16)
			Chloroform	243 (4.26); 302 sh; 311 (4.62); 352 sh (4.28); 365 (4.32)
			CH$_2$Cl$_2$	245 (4.19); 307 (4.57); 312 (4.56); 355 sh (4.16); 367 (4.18)
	ZnCl$_2$	2:1	96% ethanol	203 (4.51); 208 sh; 237 (4.54); 247 sh; 297 sh (4.78); 307 (4.81); 350 sh (4.62); 363 (4.65)
			Chloroform	245 (4.43); 310 (4.78); 353 sh (4.43); 367 (4.47)
			CH$_2$Cl$_2$	245 (4.44); 307 (4.79); 365 (4.61)
	CuCl$_2$	2:1	96% ethanol	207 (4.52); 237 (4.59); 247 sh; 299 sh (4.87); 307 (4.90); 350 sh (4.67); 362 (4.70)
			CH$_2$Cl$_2$	242 (4.77); 305 (5.12); 314 (5.11); 353 (4.85); 367 (4.86)
3c	—	—	96% ethanol	211 (3.92); 227 (3.95); 237 (3.92); 356 (4.52)
			Chloroform	363 (4.81); 380 sh
			CH$_2$Cl$_2$	245 (3.91); 360 (4.66); 380 sh
	ZnCl$_2$	2:1	96% ethanol	201 (4.59); 222 sh; 226 (4.50); 238 sh; 357 (4.94)
			Chloroform	247 (4.04); 362 (4.78)
			CH$_2$Cl$_2$	246 (3.48); 253 sh; 345 sh (3.93); 360 (3.96); 374 (3.98); 380 sh (3.96)
	CuCl$_2$	1:1	96% ethanol	201 (4.20); 225 (4.07); 238 sh; 357 (4.62)
			CH$_2$Cl$_2$	242 (3.46); 360 (3.83)

TABLE 3 (continued)

1	2	3	4	5
3d	—	—	96% ethanol	207 (4.28); 223 sh; 243 sh; 272 sh; 303 sh; 346 (4.16); 420 (4.37)
			Chloroform	247 (3.89); 340 (4.22); 408 (4.31)
			CH_2Cl_2	247 (3.95); 255 sh; 286 (3.81); 307 sh (3.95); 318 (4.00); 330sh (3.98); 403 (4.57)
	$ZnCl_2$	2:1	96% ethanol	207 (4.49); 224 (4.37); 253 (4.12); 307 (4.20); 408 (4.83)
			Chloroform	243; 263 sh; 301; 420
			CH_2Cl_2	245 (4.08); 265 (4.12); 299 (4.18); 403 sh (4.64); 419 (4.66); 437 (4.66)
	$ZnCl_2$	1:1	96% ethanol	204 (4.27); 223 sh (4.10); 253 sh; 280 (4.12); 407 (4.36)
			Chloroform	250; 285; 322; 405
			CH_2Cl_2	246 (3.66); 260 sh (3.65); 291 sh; 302 (3.71); 319 sh; 420 (4.37)
	$CuCl_2$	1:1	96% ethanol	208; 270; 307 sh; 345-360 sh; 405 sh
			Chloroform	252 sh; 278; 385-420 sh
	$CuCl_2$	2:1	96% ethanol	224 (4.48); 255 sh (4.23); 304 (4.29); 407 (4.81)
			CH_2Cl_2	253 sh; 320-333 sh (3.90); 405 (4.38)

———

* In view of the poor solubility of the copper complexes in chloroform the electronic spectra were not taken in this solvent. When plotting the spectra of saturated solutions extinction coefficients were not determined.

The electronic spectra of complexes of N-oxides **1a,b** with $CuCl_2$ of composition 1:1 in ethanol are almost identical to the spectra of N-oxides themselves, but in methylene chloride a strong hypochromic effect appears. Structures of type **7** were proposed in the literature for the analogous adducts with pyridine N-oxides [8].


7
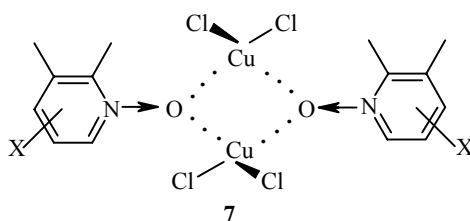
The similar complex failed to be synthesized for N-oxide **2a** even with 4-fold excess of $CuCl_2$. In our opinion this is related to steric reasons, the proximity to the N→O donor center of the styryl group which occupies a significantly larger space than a CH_3 group and especially a hydrogen atom. In this case complex formation with $CuCl_2$ must be energetically less beneficial from the side of this substituent and consequently at any donor/acceptor ratio the adduct of composition 2:1 is formed.

Especially N-oxides **3c,d** must be mentioned which, in difference to those considered above, possess firstly N→O group sterically more accessible for complex formation (the condensed system and substituent in position 2 are absent), secondly the electron-donating OCH_3 and $N(CH_3)_2$ groups located in direct resonance conjugation with the N-oxide function, but exerting no steric effect on it, and thirdly an additional heteroatom (oxygen or nitrogen) capable of forming molecular complexes of the *n*,ν-type at opposite ends of the molecule.

In difference to the other cases the complex of N-oxide **3c** with $CuCl_2$ of composition 2:1 is not obtained even with 4-fold excess of ligand. The adduct of composition 1:1 is isolated. In addition the electronic spectra of N-oxide **3c** adduct (like **1a,b** and **2a**) with $ZnCl_2$ of composition 2:1 are almost unchanged according to the position of the absorption bands at complex formation. However the values of the extinction coefficients depend markedly on the solvent used. In ethanol a hyperchromic effect is displayed, in chloroform no effect, and in methylene chloride a hypochromic effect is observed. This is possibly linked with the different ability of the given solvents to form hydrogen bonds (ethanol >> chloroform > methylene chloride) and with the presence of a methoxy group in the ligand. However for the complexes of N-oxide **3d** with $CuCl_2$ and $ZnCl_2$ of composition 2:1 a hyperchromic effect is observed in the electronic spectra in all cases. The long-wave band in ethanol undergoes a hypsochromic shift, but in chloroform and methylene chloride a bathochromic shift was observed (particularly strong with $ZnCl_2$).

The regularities observed in the electronic spectra of the adduct of N-oxide **3c** with $CuCl_2$ of composition 1:1 are similar to those described above for N-oxides **1a,b** (structure of type **7**), while on forming a complex of the same composition with N-oxide **3d** the spectra undergo large changes. The fact that this adduct has no sharp melting point, is poorly soluble even in CH_2Cl_2, and in the long-wave region of the electronic spectra there are broad absorption bands (the widening of the bands is also observed in the IR spectrum, Fig. 1), seemingly indicates complex formation both at the oxygen atom of the N→O group and at the nitrogen atom of the dimethylamino group, probably with the formation of chains of various degrees of polymerization of the type **8**.

8
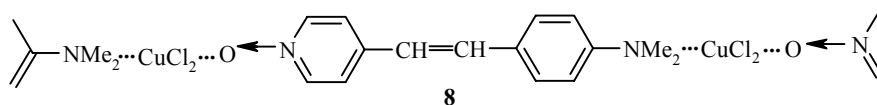
Complex with $ZnCl_2$ of composition 1:1 is successfully obtained with N-oxide **3d** and possess the same special features as the analogous complex with $CuCl_2$ (broad range of melting point, electronic spectra differing strongly from those of the initial N-oxide, containing a plateau and displaying a hypochromic effect in methylene chloride, and also reduced solubility compared with other adducts including zinc). Probably the structure of this complex is analogous to structure **8**.

The literature and our data enable the conclusion to be drawn that the structure of the stable molecular complexes of heteroaromatic N-oxides with such v-acceptors as HCl, BF_3, $ZnCl_2$, and $CuCl_2$ depends on the nature of the ligand (its basicity, electronic and steric effects of substituents, the number and type of donor
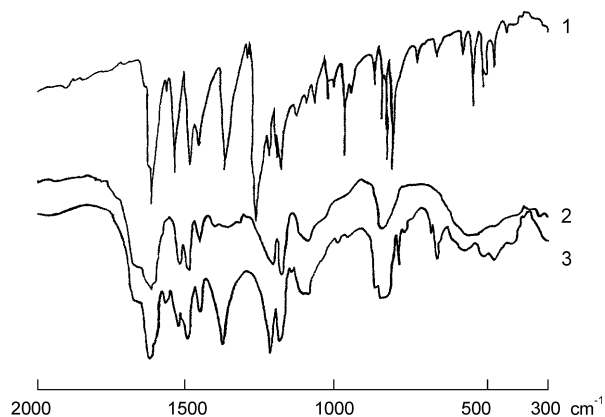
Fig. 1. The IR spectra (KBr) of 1) N-oxide **3d** and its 1:1 complex with $CuCl_2$;
2) directly after forming crystals; and 3) after standing of the reaction mixture for several days.

558

centers) and of the acceptor (hardness of the entire molecule or of its component ions) and also on the ratio of reactants in the reaction mixture and the reaction time. Reduction in the basicity of N-oxide and the hardness of the Lewis acid enables an increase in the number of types of adducts.

A detailed investigation of the complexes obtained for the first time by X-ray analysis is proposed for the future.

EXPERIMENTAL

The IR spectra were recorded on a Specord M 80 instrument in KBr disks, and the electronic absorption spectra on a Specord UV-vis in 96% ethanol, chloroform, and methylene chloride. N-Oxides of pyridine and quinoline **1a,b, 2a**, and **3c,d** were synthesized by methods described previously [3,9]. Their molecular complexes with copper and zinc chlorides were obtained by mixing warm saturated solutions of reactants in stoichiometric ratios. The precipitated solids were washed with alcohol and with ether, and dried in the air. The adduct of N-oxide **3d** with $ZnCl_2$ of composition 1:1 was obtained by drying an ethanol solution of the reactants at a ratio of 1:10. The excess of zinc chloride was washed out with alcohol.

The stoichiometric ratio of ligand and metal halide was determined by complexometric titration of Cu^{2+} or Zn^{2+} ions with Xylenol Orange as indicator in acetate buffer at pH 5 [10].

REFERENCES

1. V. P. Andreev and A. V. Ryzhakov, *Khim. Geterotsikl. Soedin.*, 1087 (1994).
2. V. P. Andreev, E. G. Kalistratova, and A. V. Ryzhakov, *Khim. Geterotsikl. Soedin.*, 516 (1996).
3. V. P. Andreev, E. G. Batotsyrenova, A. V. Ryzhakov, and L. L. Rodina, *Khim. Geterotsikl. Soedin.*, 1093 (1998).
4. A. S. Dneprovskii and T. I. Temnikova, *Theoretical Basis of Organic Chemistry* [in Russian], Khimiya, Leningrad (1991), pp. 379, 418.
5. R. G. Garvey, J. H. Nelson, and R. O. Ragsdale, *Coord. Chem. Rev.*, **3**, 375 (1968).
6. R. Whyman, D. B. Copley, and W. H. Hatfield, *J. Am. Chem. Soc.*, **89**, 3135 (1967).
7. M. R. Kidd, R. S. Sager, and W. H. Watson, *Inorg. Chem.*, **6**, 946 (1967).
8. V. P. Andreev, A. V. Ryzhakov, A. K. Morozov, O. O. Alekseeva, and L. L. Rodina, *Khim. Geterotsikl. Soedin.*, 760 (1995).
9. E. Ochiai, *Aromatic Amine Oxides*, Elsevier, New York (1967), p. 444.
10. G. Schwarzenbach and H. Flaschka, *Complexometric Titration* [Russian translation], Khimiya, Moscow (1970), 360 p.