Inorganica Chimica Acta, 29 (1978) L191–L192

New Coordination Compounds Formed from Copper(II) Halogenides and Square Planar Metal Complexes of Jäger's N_4-Macrocycles

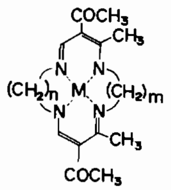
YUZO NISHIDA, HIROKI OSHIMA, and SIGEO KIDA

Department of Chemistry, Faculty of Science, Kyushu University 33, Fukuoka, 812 Japan

Received April 12, 1978

We have obtained new compounds from the reaction mixture of copper(II) halogenides, CuX_2 and the square planar metal complexes of Jäger's N_4-macrocycles [1], as shown in Figure 1. The procedure of the preparation is exemplified by that of [Ni(J-15)]·$CuCl_2$ in the followings. To a warm methanol solution (30 ml) of [Ni(J-15)] (0.001 mol) was added a warm methanol solution (20 ml) of $CuCl_2 \cdot 2H_2O$ (0.001 mol). After several hours, large needles were yielded and filtered. Other complexes were prepared by methods similar to that described above. The analytical data of the compounds obtained are listed in Table I. From the data, the new compounds can be grouped into two types; that is, one with the ratio [M(J-N)] :CuX_2 = 1:1 (A-type) and the other with the ratio 2:1 (B-type).

The spectral property of A-type compounds was found to be different from that of B-type. In Figure 2, the reflectance spectra of [Pd(J-15)]$CuCl_2$ (A-type) and $[Cu(J\text{-}14)]_2CuCl_2$ (B-type) are shown. For the latter, two bands were observed about 11500 and 18000 cm^{-1}. Considered from their positions, they are likely to be due to the d–d transitions of copper(II) ion in the $CuCl_2$ and [Cu(J-14)] chromophores, respectively. Two bands were also observed for [Pd(J-15)]$CuCl_2$. The band at 11000 cm^{-1} may be assigned to the d–d bands of copper(II) ion. The $g_\parallel$-values of A-type compounds are relatively large for a copper(II) complex (for example, $g_\parallel$ = 2.37 for [Ni(J-14)]$CuCl_2$), indicating that the ligand field around the copper(II) ion is very weak. These results are compatible with the fact that the d–d bands of copper(II) ion in A-type compounds are observed in the rather low energy region. In spite of the fact that both $CuCl_2$ and [Pd(J-15)] have no absorption bands in the range 10000–20000 cm^{-1},



M = Cu^{2+}, Ni^{2+}, Pd^{2+}

Figure 1. Metal complexes of Jäger's N_4-macrocycles, [M(J-N)]. Abbreviations are as follows: [M(J-14)], n = m = 2; [M(J-15)], n = 2, m = 3; [M(J-16)], n = m = 3.

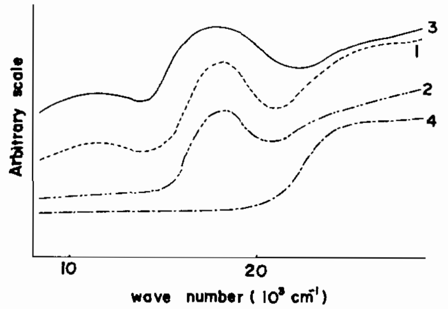


Figure 2. Reflectance spectra of the compounds. 1: $[Cu(J\text{-}14)]_2CuCl_2$. 2: [Cu(J-14)]. 3: [Pd(J-15)]$CuCl_2$. 4: [Pd(J-15)].

TABLE I. Analytical Data of the New Compounds.

Type	Compound (color)	C (%)	H (%)	N (%)	Cu (%)	Ni (%)
		found (calcd)	found (calcd)	found (calcd)	found (calcd)	found (calcd)
A	[Ni(J-14)]$CuCl_2$ (dark green)	38.67 (38.78)	4.55 (4.47)	11.28 (11.30)	12.3 (12.8)	11.4 (11.8)
	[Ni(J-15)]$CuCl_2$ (dark violet)	39.97 (40.05)	4.70 (4.73)	10.93 (10.99)	12.9 (12.5)	11.1 (11.5)
	[Ni(J-15)]$CuBr_2$ (dark green)	33.77 (34.12)	4.11 (4.04)	9.26 (9.36)	10.2 (10.6)	9.5 (9.8)
	[Pd(J-15)]$CuCl_2$ (violet)	36.09 (35.74)	4.38 (4.23)	9.63 (9.81)	11.0 (11.4)	–
B	$[Cu(J\text{-}14)]_2CuCl_2$ (brown)	44.12 (44.37)	5.01 (5.12)	12.78 (12.93)	21.7 (22.0)	–

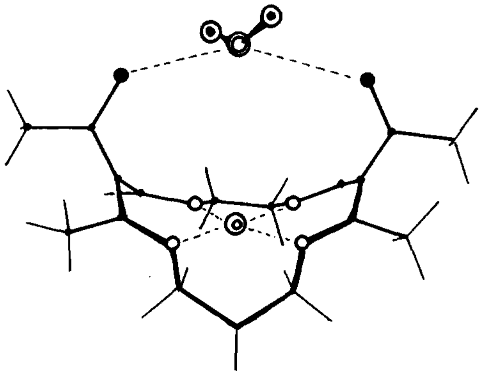


Figure 3. One of the possible structures for [Ni(J-15)]Cu-Cl$_2$. ◉,○ metal ion; ⊚ chlorine atom; ● oxygen atom; ○ nitrogen atom.

one broad band was observed for [Pd(J-15)]CuCl$_2$ at 17500 cm^{-1}. Such a new band as observed for [Pd(J-15)]CuCl$_2$ was also observed for all the A-type compounds. On the other hand, the spectra of the B-type compounds are almost the superposition of those of the parent compounds, and no new bands were observed in the 10000–25000 cm^{-1} region. These facts suggest that the structure of A-type compounds is essentially different from that of B-type compounds.

The only possible bonding site for copper(II) ion in Jäger's N$_4$-macrocycles may be the oxygen atoms in acetyl groups. Judging from the electron-withdrawing property of the oxygen atom in the acetyl group, the oxygen atom may possess enough electron density to coordinate to a copper(II) ion.

Various possible structures can be assumed for the A-type compounds, *e.g.*, a discrete dimer, one-dimensional- and two-dimensional infinite chains, *etc.* The fact that the new absorption was observed in the A-type and not in the B-type compounds suggests the presence and the absence of the direct interaction between metal ions in the A-type and B-type compounds, respectively. One of the possible structures of A-type (exemplified by [Pd(J-15)]CuCl$_2$) is depicted in Figure 3. The conformation of the [Ni(J-15)] moiety is consistent with the results of the X-ray analysis of the compound similar to [Ni(J-15)] [2]. Furthermore, the examination of Dreiding Stereomodels revealed that two acetyl oxygen atoms can approach to each other up to 4.0 Å, so that the structure of Figure 3 is a possible one. In order to confirm the above view, we have begun to determine the crystal structure of an A-type compound by X-ray analysis.

References

1 Copper(II) and nickel(II) complexes of Jäger's N$_4$-macrocycles were prepared according to the methods described in the literature: E. G. Jäger, *Z. Chem.*, *8*, 30, 392, 475 (1968). New palladium(II) complexes of Jäger's N$_4$-macrocycles were prepared in this study.

2 P. W. R. Corefield, J. D. Mokren, C. J. Hipp and D. H. Busch, *J. Am. Chem. Soc.*, *95*, 4465 (1973).