Bi- and Tri-Nuclear Copper(II) Complexes Derived from Bi- and Tetra-dentate Schiff-base Complexes

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(Received April 5, 1969)

As an extension of a previous study,[1] we have prepared a large number of copper(II) complexes with bidentate or tetradentate salicylideneimines and the appropriate anions. Tow types of complexes were prepared; the first (Group A), by the reaction of $\mathrm{Cu(Sal\cdot N{-}R)_2}$ and cupric chloride or nitrate in hot ethanol, where $\mathrm{Sal\cdot N{-}} = \cdot\overset{1}{\mathrm{O}}\cdot\mathrm{C_6H_4}\cdot\overset{2}{\mathrm{C}}\mathrm{H{=}N}\cdot$ and R=various alkyl or substituted phenyl groups; the second (Group B), from the reaction of $\mathrm{Cu(Sal\cdot N{-}CH_2CH_2{-}N\cdot Sal)}$ with cupric chloride, nitrate, or perchlorate under similar conditions. Nearly all of these complexes have subnormal magnetic moments, suggesting the presence of a strong intramolecular spin-spin interaction. Most of them seem to be binuclear, $\mathrm{[Cu(Sal\cdot N{-}R)Cl]_2}$; however, some complexes of the group B were found to be trinuclear when cupric perchlorate was used.

One of the most significant features of the chloro-complexes of the group A is the existence of a linear relation between the d–d band positions, $\bar{\nu}_{\max}$ ($\mathrm{cm^{-1}}$, kK), and the magnetic moments, $\mu_{\mathrm{eff}}^{25^\circ\mathrm{C}}$ (B.M.), "lower moments——higher energies of d–d bands," where R=alkyl(10—14 kK, 1.5—0.9 B.M.) and substituted phenyl groups (11—12.5 kK, 1.5—1.1 B.M.), which is the same relation as that observed for the binuclear copper(II) halide complexes with substituted pyridine *N*-oxides (9—13.5 kK, 1.2—0.2 B.M.).[1] For *N*-phenyl-complexes *ortho*-substituents in the *N*-phenyl group increase the energies of the singlet-triplet separation and the d–d bands, irrespective of the polar nature of the substituents ($\mathrm{CH_3}$, Cl, and $\mathrm{NO_2}$). This same shielding effect of *ortho*-substituents was found previously for the pyridine *N*-oxide complexes. The chloro-complexes of Group A are mostly dark brown in color; a few, however, are orange with a broad band at longer wavelengths (9—11 kK). The orange complexes do not obey the above linear relation, suggesting a different structure even though they have the same composition as the binuclear complexes, $\mathrm{Cu(Sal\cdot N{-}R)Cl}$. They also have the lowest moments of the two groups; for example, when $\mathrm{R=CH_3}$ (0.90 B.M. orange; 1.5 B.M. brown) and $\mathrm{R=CH_2CH_2CH_2OH}$ (1.06 B.M.), *o*- and *p*-$\mathrm{NO_2}$-phenyl (1.06 and 0.97 B.M.), and $\mathrm{Cu(5\text{-}Cl{-}Sal\cdot N{-}CH_3)Cl}$ (0.95 B.M.).

The nitrato-complexes of Group A are, in general, green with the d–d bands at much shorter wavelengths (13.5—15.5 kK) than those of the corresponding chloro-complexes (10—14 kK). They seem to have a phenolic oxygen-bridged binuclear structure; this is based on the observed chemical formula, $\mathrm{Cu(Sal\cdot N{-}R)NO_3}$, the molecular-weight determination by osmotic pressure measurement, the observation of a bridging phenolic C–O band at 1550—1560 $\mathrm{cm^{-1}}$,[2,3] and the low magnetic moments, 1.1—1.4 B.M. Some nitrato-complexes with R=3-$\mathrm{CH_3}$– and 3-Cl-phenyl (green) or *t*-butyl group (greenish brown) have normal magnetic moments, 1.7—1.8 B.M. These complexes show a non-bridging phenolic C–O band at *ca.* 1530 $\mathrm{cm^{-1}}$, suggesting a monomeric structure.[2,3] However, when R=isopropyl, a trinuclear complex, $\mathrm{2Cu(Sal\cdot N{-}R)_2\cdot Cu(NO_3)_2}$, was produced, with a normal moment (1.84 B.M. at 19°C). The nitrato-complexes with subnormal magnetic moments did not show the linear relation between $\mu_{\mathrm{eff}}^{25^\circ\mathrm{C}}$ and $\bar{\nu}_{\max}$ which was observed for the corresponding chloro-complexes. This suggests that the dimeric structure of nitrato-complexes differs from that of chloro-complexes.

The binuclear chloro- and nitrato-complexes produced by reaction (2) (Group B) revealed two bands, at 18.5—19.5 kK and 10—11.5 kK, indicating that the environment of the two copper atoms in the molecule is greatly different. However, the bands of the chloro-complexes appeared at longer wavelengths than those of the corresponding nitrato-complexes, and the former exhibited a smaller magnetic interaction (1.5 B.M.) than the latter (1.2—1.3 B.M.). This is essentially the same trend as the linear relation observed for the chloro-complexes of Group A.

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[1] Y. Muto, M. Kato, H. B. Jonassen and L. C. Cusachs, This Bulletin, **42**, 417 (1969).

[2] S. J. Gruber, C. M. Harris and E. Sinn, *J. Inorg. Nucl. Chem.*, **30**, 1805 (1968).

[3] C. M. Harris and E. Sinn, *ibid.*, **30**, 2723 (1968).