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Communications

Copper Derivatives of N,N'-Bis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyl]hydrazine

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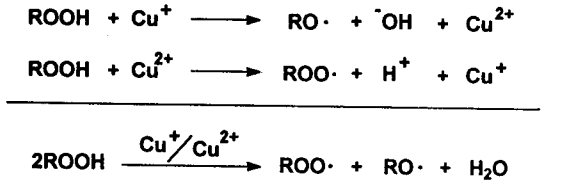
Complex-forming agents for copper ions are of interest because of their effectiveness as copper deactivators in crosslinked low density polyolefins.[1] Copper, one of the transition metals which have two discrete oxidation states involving one electron redox potential of low energy barrier, can act as an accelerator for the oxidation of polyolefins (polymer degradation).[1,2] One of the possible mechanisms involving in the degradation processes is that copper ions catalytically decompose alkylperoxide to alkoxy radical or alkylperoxy radical which can initiate radical chain reactions of polyolefins as shown in Scheme 1. For the particular use of polyolefins applying to an electric cable, it is important to develop additives which can act not only as antioxidants but as copper deactivators. Many antioxidants have been developed for this purpose and some of them are commercially available.[1-3] Recent studies tested for several groups of chelating agents have revealed that acylated hydrazines with bulky substituents are highly effective for copper deactivators by measuring the oxygen-uptake induction periods.[3] Fundamental chemistry concerning the complexation mechanism is, however, still the subject of debate. Reported here is unprecedented example of copper derivatives obtained from the reactions of copper ions and N,N'-bis[3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionyl] hydrazine (BPNH), which provides some important information about the bonding mechanism for the complexation between copper ions and BPNH.

As a model compound for this study, N,N'-bis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyl]hydrazine (BPNH) has



Scheme 1.

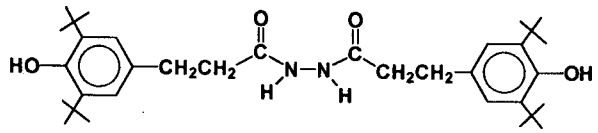


Figure 1. Structure of BPNH.

been chosen for chelating agent (Figure 1). Reactions of BPNH with $CuX_2 \cdot (Solvent)_n$ (X=NO_3, OTf) in acetone gave green suspension, from which deep-green solid was isolated by vacuum filtration. We tentatively formulate this product is a bis-chelating dimeric complex $[Cu(BPN)]_2$ (BPN=N,N'-deprotonated BPNH, see Figure 2) (vide infra). The products obtained from the two independent reactions using Cu(II) ions having different counter anion of NO_3^- or ^-OTf, are the same each other. The IR spectrum of each product shows all the identical absorption peaks each other in the region of 4000-400 cm^{-1}, but no band for the corresponding counter anion NO_3^- or ^-OTf. We expect these bands around 1380 cm^{-1} and 1260 cm^{-1} with strong intensities, respectively. The strong intense peak at 1515 cm^{-1} in the IR spectrum is assigned to the ν(CO), which is considerably decreased by the comparison with that of the free ligand BPNH.[4]

The IR spectrum shows no absorption band due to ν(N-H), but shows the absorption band due to the ν(OH) observed at 3643 cm^{-1}. A considerable decrease for the ν(CO), the disappearance of the ν(N-H), and no absorption band for the counter anion NO_3^- or ^-OTf in the IR spectrum indicate that the complex is a copper derivative of N,N'-deprotonated BPN which is coordinated through O and N.[5] The complex is nearly insoluble in most organic solvent and only sparingly soluble in DMSO. Recrystallization from DMSO and ether gave analytically pure complex. The microanalyti-

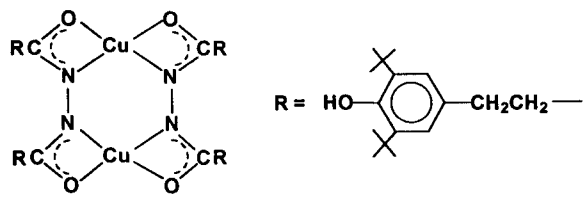
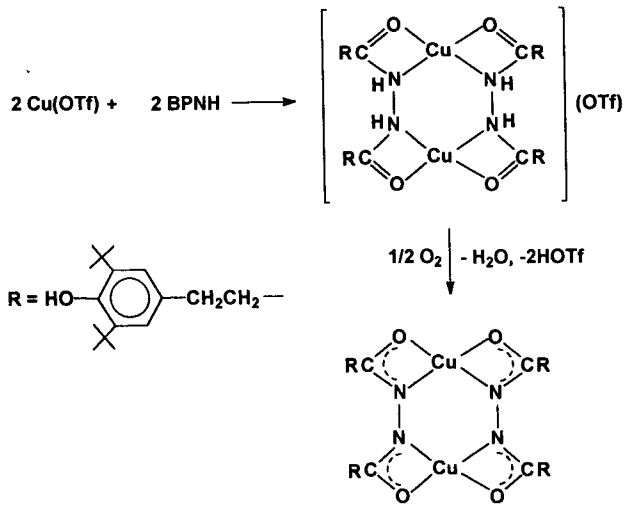


Figure 2. Proposed structure of $[Cu(BPN)]_2$.



Scheme 2. Plausible reaction pathway in the reaction of Cu(I) and BPNH.

cal data indicates that the compound is composed of BPN and Cu in the ratio of 1.[6] For the formulation of this complex, the FAB/MS spectrum of a DMSO solution of the complex has been obtained. A parent molecular ion for the dimer was not detected in the spectrum. However, we can observe a fragment at m/z=1197.6, which is likely due to the loss of C_2H_5 from the parent dimeric molecule $[Cu(BPN)]_2$.[7] The fragment for the protonated free BPNH ion has also been observed at m/z=553.4. We now formulate this complex is a N,N′-dehydrogenated dimeric copper derivative $[Cu(BPN)]_2$.[8] A structure of this bis-chelating dimeric complex is suggested as shown in Figure 2. The formation of $[Cu(BPN)]_2$ can be explained by a sequence of reactions involving the coordination of BPNH to the Cu(II) center by ligand displacement, and then dehydrogenations from the coordinated BPNH followed by eliminations of HX ($X=NO_3^-$ or ^-OTf).

When BPNH reacted with Cu(OTf), a pale blue compound has been obtained. The IR spectrum of this compound shows absorption bands due to the ν(NH) at 3193 cm^{-1}, the ν(CO) at 1597 cm^{-1}, and the ν(SO) at 1254 cm^{-1}, which are attributed to a new compound. The compound obtained from the reaction is contaminated with small amount of $[Cu(BPN)]_2$ evidenced by the observation of the ν(CO) at 1515 cm^{-1} in its IR spectrum. The new compound obtained from the reaction of BPNH and Cu^+ ion is likely formulated $[Cu_2(BPNH)_2](OTf)_2$ (vide infra).[9] Repeated preparation of this compound even at highly deaerated atmosphere can not prevent the formation of small amount of $[Cu(BPN)]_2$. Attempt to obtain ^1H NMR spectrum of the complex could not be reliable because of the line broadenings due to the contamination of paramagnetic Cu(II) complex $[Cu(BPN)]_2$. When this pale blue compound dissolved in acetone in the presence of oxygen, the complex $[Cu(BPN)]_2$ slowly precipitated out from the solution, and this Cu(II) complex was isolated as a whole product within 12 hrs. These results have following implications. The reaction of BPNH with Cu^+ ion gives a simple addition product $[Cu_2(BPNH)_2]^{2+}$. The oxidation of this Cu(I) complex by molecular oxygen gives a copper(II) complex $[Cu_2(BPNH)_2]^{4+}$, which immediately converts into the dehydrogenated derivative $[Cu(BPN)]_2$. Reaction pathway involving these processes is shown in Scheme 2.

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2. (a) Osawa, Z. *Polym. Deg. Stab.* **1988**, *20*, 203 and references therein. (b) Chirinos-Padron, A. J.; Hernandez, P. H.; Suarez, F. A. *Polym. Deg. Stab.* **1988**, *20*, 237.
3. Schipschack, K.; Beger, J.; Neumann, R.; Wagner, H. *Angew. Macromol. Chemie* **1992**, *199*, 103.
4. For the comparison of the characteristic absorption bands; IR data for BPNH (nujol mull); ν(OH)=3616 cm^{-1} (m), ν(NH)=3237 cm^{-1} (m), ν(CO)=1670 cm^{-1} (vs, sh). IR data for $[Cu(BPN)]_2$ (nujol mull); ν(OH)=3643 cm^{-1} (m), ν(CO)=1515 cm^{-1} (vs, sh).
5. Although intramolecular dehydrogenation of coordinated amines to giveimines is well known, the N,N′-dehydrogenation of dialkylhydrazines upon coordination to tungsten and chromium has been recently reported; see Ackerman, M. N.; Hardy, L. C.; Xiao, Y. Z.; Dobmeyer, D. J.; Dunal, J. A.; Felz, K.; Sedman, S. A.; Alperovitz, K. F. *Organometallics* **1986**, *5*, 966. Macrocyclic complexes containing mixed N,O-donor ligands are also common; Henrick, K.; Tasker, P. A.; Lindoy, L. F. *Prog. Inorg. Chem.* **1985**, *33*, 1.
6. Anal. Calcd for $C_{68}H_{100}N_4O_8Cu_2$: C, 66.47; H, 8.20; N, 4.56. Found: C, 66.74; H, 8.34; N, 4.40.
7. The calculated value of the exact mass for $[Cu(BPN)]_2$ is 1226.6.
8. A higher order of oligomeric compound $[Cu(BPN)]_n$ (n>2) can not be excluded.
9. For the comparisons of the IR data with BPNH and $[Cu(BPN)]_2$; see ref 4.