Polish J. Chem., **75**, 1203–1208 (2001)

μ-phth-μ-X Bridged Dicobalt(II) Complexes: Synthesis, Properties and Catalase-Like Activity

by J. Gao and S.H. Zhong[*]

College of Chemical Engineering and Technology. Tianjin University, Tianjin 300072, China

(Received December 28th, 2000; revised manuscript February 23rd, 2001)

μ-phth (phthalic acid dianion), having two isolated metal-binding groups, together with X ligand (X = $CH_3CO_2^-$, $CF_3CO_2^-$ and Ph-CO_2^-) formed dicobalt(II) complexes $[Co_2(II)(\mu\text{-phth})(\mu\text{-}CH_3CO_2^-)(bipy)_2]ClO_4$ (**1**), $[Co_2(II)(\mu\text{-phth})(\mu\text{-}CF_3CO_2^-)(bipy)_2]ClO_4$ (**2**) and $[Co_2(II)(\mu\text{-phth})(\mu\text{-Ph-}CO_2^-)(bipy)_2]ClO_4$ (**3**). Their structure was characterized spectroscopically and magnetically, presenting a μ-phth-μ-X-bridged dinuclear structure. The pair of cobalt ions bridged by CH_3COO undergoes antiferromagnetic coupling. Catalytic properties for H_2O_2 dismutation are reported for complex **1–3**.

Key words: complexes, hydrogen peroxide, catalase-like activity, synthesis

Transition metal complexes with extended bridging structures are currently interesting topics due to the spin-coupling and charge transfer between metal ions and bridging-ligand in the domain of metalloenzymes [1]. Dinuclear cores are commonly existing in natural system [2] and chemical model approaches by use of simple metal complex are becoming important. Schiff base ligands [3,4] are normally being used to create the dinuclear core structure. As phthalate dianion (μ-phth) is a good dinucleating candidate and its crystal structure has been defined by well established work [5], we try to use it to design a more simple Cat-like model system.

Dinuclear cores bridged by one oxygen-containing (oxo, hydroxo or water) and one or two carboxylate groups are widely known in biosites such as haemerythrin [6], ribonucleotide reductase [7] and phospholipase C [8], *etc*. A similar dinuclear core is proposed for the active site of Mn–CAT [9]. Model system of μ-phenoxo-bis-(μ-carboxylato) dinuclear complex relevant to μ-oxo-bis(μ-carboxylato) cores are found to have catalase activity [10]. In this study, μ-phth were used to synthesize dicobalt(II) core structure, which allow the involvement of oxygen-containing bridge (μ-R-CO_2) between a pair of metal ions. Significantly, these complexes are found to have catalase-like activity comparable to similar Mn–CAT model system [11].

---

[*] Corresponding author: E-mail: shzhong@public.tpt.tj.cn; Fax: 86-022-23358329; Tel: 86-022-27404026

EXPERIMENTAL

All reagents used are of analytical grade and purchased from the Peking Chemical Company in China.

Preparation of $[Co_2(II)(\mu\text{-phth})(\mu\text{-}CH_3COO)(bipy)_2]ClO_4$ (1): In dinitrogen-flushed methanol solution (10 ml) containing phthalic acid (33.2 mg, 0.2 mmol), bipy (62.5 mg, 0.4 mmol) and triethylamine (0.4 mmol), a solution of Co $(ClO_4)_2 \cdot 6H_2O$ (146.3 mg, 0.4 mmol) in methanol (15 ml) was added and kept under magnetic stirring, red solution and few red microcrystal were obtained. To this solution was added CH_3COONa (0.2 mmol). The red suspension was turned into brown, after the mixture was stirred for 2 h. After no further color change could be observed, the final product was separated, washed with absolute methanol and diethyl ether three times and dried in vacuum.

Preparation of $[Co_2(II)(\mu\text{-phth})(\mu\text{-}CF_3COO)(bipy)_2]ClO_4$ (2): Following a similar reaction procedure as stated in the previous section, by using CF_3CO_2Na instead of CH_3CO_2Na. Brown microcrystals were obtained.

Preparation of $[Co_2(II)(\mu\text{-phth})(\mu\text{-Ph-COO})(bipy)_2]ClO_4$ (3): Following a similar reaction procedure as stated in the previous section, but using Ph-CO_2Na instead of CH_3CO_2Na. Yellow-brown microcrystals were obtained.

Chemical analyses confirmed the compositions.

Measurement: Analysis for C, H, and N were carried out on a Perkin-Elmer analyzer, Model 240 and metal contents were determined by EDTA titration. The infrared spectra were recorded with a Perkin–Elmer IR spectrophotometer, Model 983G, using KBr-disks. Electronic spectra (in methanol) were measured on a Shimadzu UV-240 spectrophotometer. Solution electrical conductivity measurements were made with a DDS–11A conductometer. Variable-temperature magnetic susceptibilities were measured on a SQUID susceptometer (sensitivity m = 10^{-6} emu). Diamagnetic corrections were made with Pascal's constants for all the constituent atoms, and the magnetic moments were calculated using $\mu_{eff} = 2.828(X_M T)^{1/2}$.

Study of catalase-like activity: All reactions were carried out at 20°C and in a 50 ml reactor containing a stirring bar under air. To methanol (14.85 ml) was added th the separation between υ_{as} and υ_s has often been used to diagnose the coordination models of the carboxylato groups. The separation values between υ_{as} and υ_s for complexes **1–3** are all smaller than 200 cm^{-1} suggesting a bidentate mode for both carboxylato groups [13]. For these complexes, ClO_4^- vibrations at 1095 and 630 cm^{-1} are observed. These data are consistent with the molar conductance measurements.

The absorption spectrum for complex **1** is given in Fig.1. In visible range, the expected weak d-d transitions were observed by a broad shoulder at *ca*. 540 nm, which is tentatively ascribed to the ligand to metal charge transfer of CH_3CO_2→Co(II). Another CT band was also obscured at ca. 250 nm and can be attributed to N→Co(II) or O→Co(II) transfer. These data indicated a five coordinate Co(II) chromophore with distorted square-pyramidal configuration. Based on the discussion above, complexes **1–3** are proposed to have μ-X bridged dinuclear structure with μ-phth as a supporting fragment. In these complexes phthalic acid dianion connects two cobalt(II) ions in a bis-bidentate fashion and metal ions in a square pyramidal environment, resulting a heterocyclic structure shown as Fig. 2.

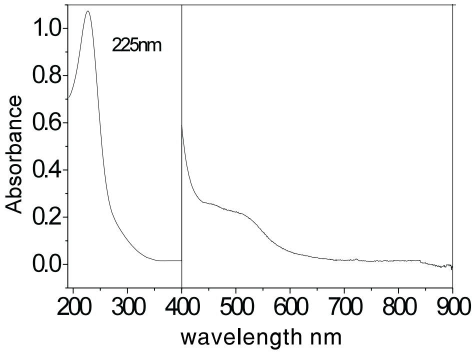
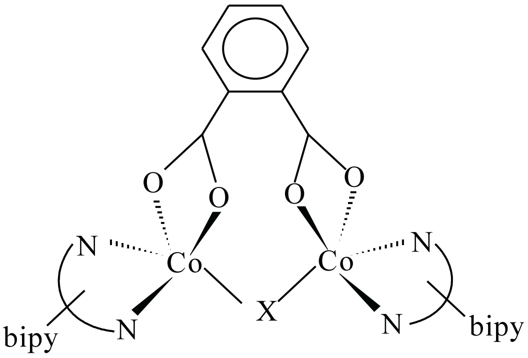


Figure 1. Electronic spectra of complexes **1**.



X = CH_3COO^-, CF_3COO^- or Ph-COO^-

Figure 2. Proposed structures of the complexes.

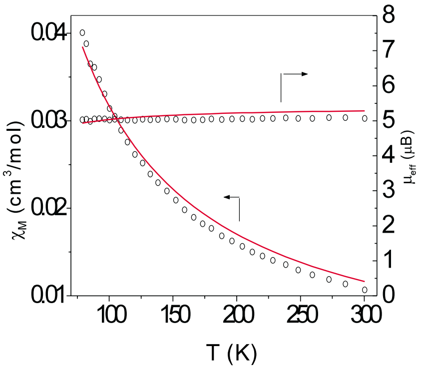


Figure 3. Temperature variation of magnetic moment of complex **1**.

Magnetic properties and magnetic structural correlations: Variable-temperature magnetic susceptibility data for complex **1** were collected in the 77–300 K ranges. The M *versus* T plot is shown in Figure 3. The magnetic moments decrease with decreasing temperature, implying the existence of an antiferromagnetically coupling of Co(II)–Co(II) pairs. In order to understand quantitatively the spin-exchange interaction, the analysis was carried out with the susceptibility equation based on the Heisenberg spin-exchange operator $H = -J \cdot S_1 \cdot S_2$. The molar susceptibility of the Co–Co ($S_1 = S_2 = 3/2$) system was calculated by the van Vleck equation [14]

$$\chi_M = \frac{2Ng^2\beta^2}{k(T-\theta)}[14+5\exp(-6J/kT)+\exp(-10J/kT)]/[7+5\exp(-6J/kT)+ 3\exp(-10J/kT)+\exp(-12J/kT)](1-\rho)+\frac{0.9375g^2}{T}\rho$$

where χ_M denotes the susceptibility per binuclear complex, ρ denotes the fraction of mononuclear paramagnetic impurity, and other symbols have their usual meaning. As shown in Fig. 3, good fit to the experimental data were attained. The magnetic parameters thus determined are $J = -15.0$ cm^{-1}, $g = 1.97$, $\rho = 0.005$. μ-CH_3CO_2 is corresponding to the spin-coupling between the cobalt ions, since the exchanging integral of μ-phth bridged complexes is negligible or positive [5]. It is well established that the type and magnitude of magnetic exchange interactions in dinuclear complexes depend on bridge identity, the distance between metal ions, the band angles at the bridging atom, the dihedral angle between the planes containing the cobalt(II) ions, the metal-bridging ligand bond length [15]. Even though our effort to obtain single-crystal of complex **1** was unsuccessful, the quantitative difference of the spin-coupling between the complex **1** and close related $[Co_2THPH(bipy)_4](ClO_4)_2$ [16] is easy to illustrate. For complex **1**, two cobalt(II) ions in two planes are connected by μ-CH_3CO_2 bridge, when the metal ions moves towards the same plane, thus increase the antiferromagnetic interaction.

Fig

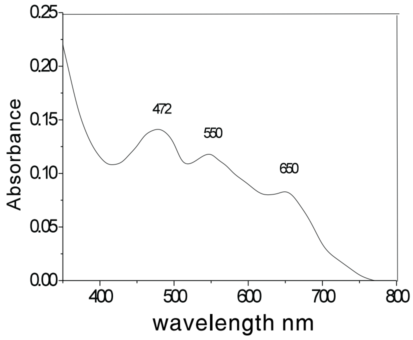


Figure 5. Visible spectrum changes in the catalytic reaction of H_2O_2 by complex **1**.

become reddish-brown and showed weak bands at 472 ($^1A_{1g} \rightarrow {}^1T_{2g}$), 550 ($^1A_{1g} \rightarrow {}^1A_{2g}$) and 650 nm ($^1A_{1g} \rightarrow {}^1E_g$) (Fig.5), which suggest the involvement of Co(III) species in the catalytic process. This result might clear that the Co(III) complex is more stable than the Co(II) complex, while the oxygen presence and that the real active sites for H_2O_2 decomposition is the Co(III) species. To our knowledge these are the first μ-phth-μ-X bridged dicobalt(II) complexes, which show the catalase-like reactivity.

REFERENCES

1. Willet R.D., Gatteschi D. and Hahn O. (Editor), *Magneto-Structural Correlation in Exchange-Coupled Systems,* p. 523. Reidel, Dordrecht (1985).
2. Fenton D.E. and Okawa H., *Perspectives on Bioinorganic Chemistry,* eds. Hay R.W., Dilworth J.R. and Nolan K.B., JAI Press, London, **2**, p. 81–138 (1993).
3. Mathur P., Crowder M. and Dismukes G.C., *J. Am. Chem. Soc.,* **109,** 5227 (1987).
4. Higuchi C., Sakiyama H., Okawa H., Isobe R. and Fenton D.E., *J. Chem. Soc., Dalton. Trans.*, 1097 (1994).
5. Shakhatreh S.K., Bakalbassis E.G., Brudgam I., Hartl H., Mrozinski J. and Tsipis C.A., *Inorg. Chem.,* **30**, 2801 (1991).
6. Holms M.A., Letrong I., Turkey S., Sleker L.C. and Stenkamp R.E., *J. Mol. Biol.,* **218,** 583 (1991).
7. Nordlund P., Sjoberg B.M. and Eklund H., *Nature* (London), **345**, 593 (1990).
8. Hough E., Hansen L.K., Birknes B., Jyngo K., Hansen S., Hordvik A., Little C., Dodson E.J. and Derewenda Z., *Nature* (London), **338**, 357 (1989).
9. Wiehhardt K., *Angew, Chem. Int. Ed. Engl.*, **28**, 1153 (1989).
10. Sakiyama H., Tamaki H., Kodera M., Matsumoto N. and Okawa H., *J. Chem. Soc. Dalton Trans.*, 591 (1993).
11. Higuchi C., Sakiyama H., Okawa H. and Fenton D.E., *J. Chem. Soc., Dalton Trans.*, 4015 (1995).
12. Geary W.J., *Coord. Chem. Rev.,* **7**, 81 (1971).
13. Bakalbassis E., Gouterou J., Jeannin S., Jeannin Y. and Kahn O., *Inorg. Chem*., **23**, 4291 (1984).
14. Ball P.W. and Blake A.B., *J. Chem. Soc., Dalton Trans.,* 852 (1974).
15. Chavlot M.F., Jeannin S., Jeannin Y., Kahn O., Lucrece-Abaul J. and Martin-Frere J., *Inorg. Chem.,* **18,** 1675 (1979).
16. Ma S.L., Liao D.Z. and Jiang Z.H., *Synth. React. Inorg. and Met-Org*., **24**, 137 (1994).
17. Menage S., Vincent J.M., Lambeaux C., Chottard G., Grand A. and Fontecave M., *Inorg. Chem.*, **32**, 4766 (1993).