TABLE XI

THERMODYNAMIC PROPERTIES FOR THE MIXED-COMPLEX FORMATION REACTION

$$\tfrac{1}{2}\text{CuA}_2 + \tfrac{1}{2}\text{CuB}_2 \overset{K_M}{\rightleftharpoons} \text{CuAB}$$

IN AQUEOUS SOLUTION AT 25°

Systems	Log K_M	$-\Delta G_M$, kcal mol^{-1}	ΔH_M, kcal mol^{-1}	ΔS_M, cal deg^{-1} mol^{-1}	$-$Log K_s	ΔG_s,[a] kcal mol^{-1}	ΔS_s,[b] cal deg^{-1} mol^{-1}	$\Delta G_{M,e}$, kcal mol^{-1}	$\Delta H_{M,e}$, kcal mol^{-1}	$\Delta G_{M,c}$, kcal mol^{-1}	$\Delta H_{M,c}$, kcal mol^{-1}
Cu + gly + α-ala	0.13	0.19	0.42	2.0	0.17	0.22	0.6	−0.13	0.05	0.35	0.37
Cu + gly + val	0.16	0.22	0.35	1.9	0.14	0.19	0.5	−0.11	0.04	0.30	0.31
Cu + gly + ser	−0.14	−0.17	0.40	0.8	0.44	0.58	−0.6	+0.15	−0.05	0.45	0.45
Cu + α-ala + val	0.40	0.54	−0.02	1.7	−0.10	−0.13	0.3	−0.07	0.02	−0.06	−0.04
Cu + α-ala + ser	0.22	0.29	−0.03	0.9	0.08	0.12	−0.5	0.11	−0.04	0.01	0.01
Cu + val + ser	0.17	0.23	−0.04	0.6	0.13	0.18	−0.8	0.17	−0.06	0.01	0.02

[a] $\Delta G_s = \Delta G_M + R \ln 2$. [b] $\Delta S_s = \Delta S_M - R \ln 2$.

seen from the positive $\Delta H_{M,c}$ (or $\Delta G_{M,c}$) values, and (ii) the differences in the degree of solvation between the more polar mixed complex and the symmetrical binary complexes. It can be seen in Table XI that when serine is one of the competing ligands, ΔS_S ($= \Delta S_M - R \ln K_{stat}$) values are negative for the mixed-complex formation. Serine has an electron-withdrawing hydroxyl group which effectively reduces its σ-donor properties. When a covalent mixed complex is formed between serine and glycine, α-alanine, or valine, there is an increase in the strength of the bond formed by the ligand with greater σ-donor properties. At the same time, the bond formed by the weaker σ donor, serine, becomes progressively less strong relative to the strength of the same bond in the nonmixed complex. The resulting redistribution of the electron density leads to a change in the polarity of the individual bonds.

In competition with a stronger σ donor such as glycine, α-alanine, or valine, the resulting mixed complex involving serine is more polar than either of the nonmixed binary complexes. This is reflected in a greater degree of solvation of the complex and a lower entropy change.

Acknowledgment.—We wish to thank the National Science Foundation for financial support through Grant No. GP-9231.

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Out-of-Plane Bonding in the α and β Forms of Bis(8-hydroxyquinolinato)copper(II)

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Received February 3, 1972

The magnetic susceptibilities of the α and β forms of bis(8-hydroxyquinolinato)copper(II) have been measured from 4.2 to 62°K for the α form and 3.2 to 77°K for the β form. The magnetic data indicate that there is little spin–spin coupling between the copper(II) ions in either the chain structure (α form) or the dimeric structure (β form). The results suggest that out-of-plane copper–oxygen distances of 2.8 Å or greater are too long to transmit significant spin–spin interactions.

Introduction

Suito and Sekido[1] first prepared two forms of $Cu(8\text{-}OQuin)_2 \cdot 2H_2O$ by reacting cupric sulfate with 8-hydroxyquinoline (8-OQuin) in water at various temperatures and concentrations. Fanning and Jonassen[2] prepared the anhydrous complexes and studied their room temperature magnetic properties and infrared spectra. Frazer, *et al.*,[3] measured the magnetic susceptibilities as a function of temperature for both forms down to 88°K. The crystal structure of the α form was determined by Hoy and Morriss[4] and the structure of the β form by Palenik.[5] The structure of the α form, depicted in Figure 1, consists of a chain of essentially planar $Cu(8\text{-}OQuin)_2$ molecules. Each copper atom is six-coordinate and is weakly coordinated in the apical positions by oxygen atoms from neighboring molecules; the copper–oxygen out-of-plane distance being 3.32 Å. The in-plane copper–oxygen distance is 1.94 Å. The β form exists as a dimer-like unit (see Figure 2) in which copper is five-coordinate and the copper–oxygen out-of-plane distance is 2.83 Å. The copper–oxygen in-plane distance of 1.93 Å is almost identical with that observed for the α form.

Since it has been shown previously[6,7] that out-of-plane interactions in similar complexes can be important, we have undertaken a study of the low-temperature magnetic and spectral properties of both the α and β forms of $Cu(8\text{-}OQuin)_2$. This was done as a part of

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[1] E. Suito and E. Sekido, *Proc. Jap. Acad.*, **33**, 196 (1957).

[2] J. C. Fanning and H. B. Jonassen, *J. Inorg. Nucl. Chem.*, **25**, 29 (1963).

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[5] G. J. Palenik, *ibid.*, **17**, 687 (1964).

[6] W. E. Hatfield, J. A. Barnes, D. Y. Jeter, R. Whyman, and E. R. Jones, *J. Amer. Chem. Soc.*, **92**, 4982 (1970).

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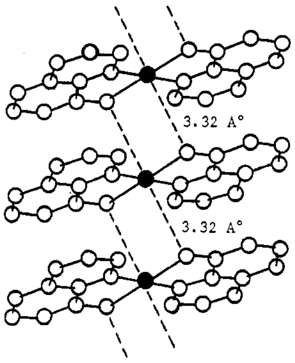

Figure 1.—The structure of α-bis(8-hydroxyquinolinato)copper(II).

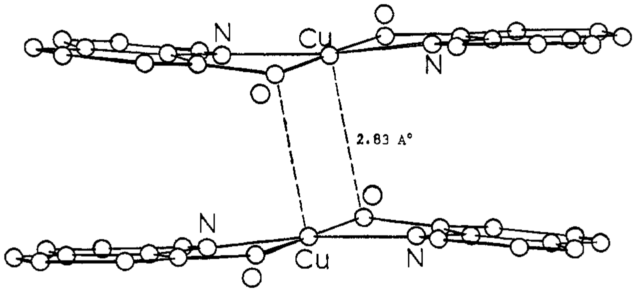

Figure 2.—The structure of β-bis(8-hydroxyquinolinato)copper(II).

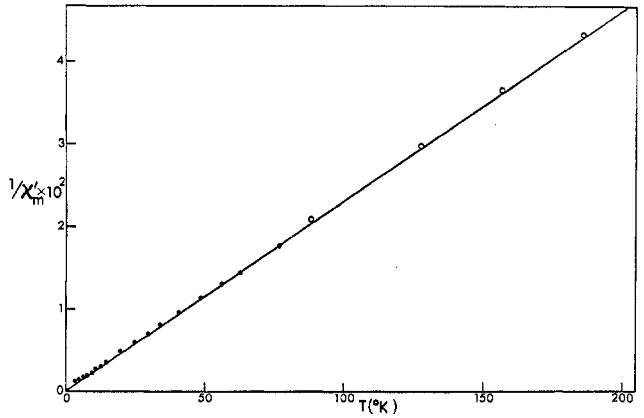

Figure 3.—Inverse molar susceptibility of β-bis(8-hydroxyquinolinato)copper(II) as a function of temperature. Closed circles represent data from this work; open circles represent data from reference 3.

the continuing investigation in this laboratory of the effects of out-of-plane bonding in chains and dimers as well as other multimetallic systems.

Experimental Section

Both forms of bis(8-hydroxyquinolinato)copper(II) were prepared by the method of Fanning and Jonassen.[2] *Anal.* Calcd for α-$(C_9H_6NO)_2Cu^{II}$: C, 61.46; H, 3.44; N, 7.96. Found: C, 61.33; H, 3.42; N, 7.87. Calcd for β-$(C_9H_6NO)_2Cu^{II}$: C, 61.46; H, 3.44; N, 7.96. Found: C, 61.2; H, 3.28; N, 7.81.

Magnetic susceptibilities were determined using a Princeton Applied Research Model-155 vibrating sample magnetometer of the Foner[8] type. Corrections were applied for the diamagnetism[9] of each sample and for a temperature-independent paramagnetism of 60×10^{-6} cgsu. Further corrections were made

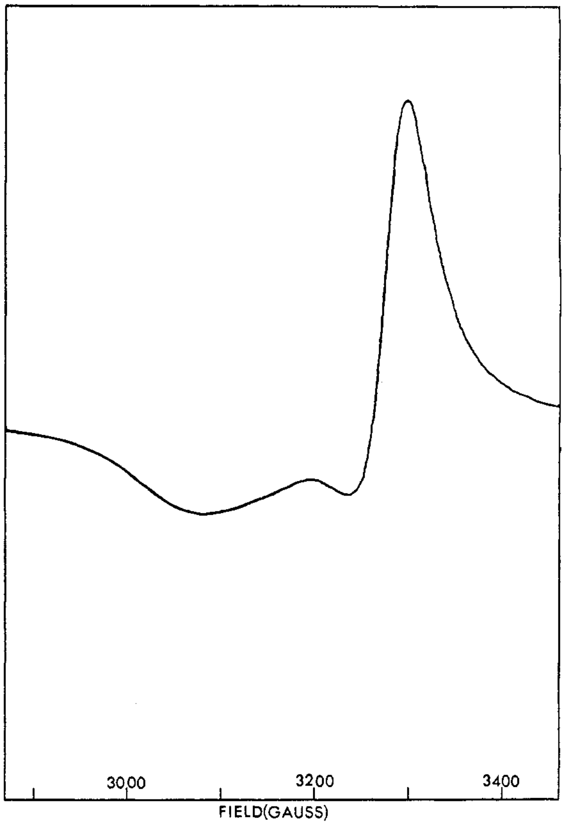

Figure 4.—Epr spectrum of α-bis(8-hydroxyquinolinato)copper(II) (powder), $T = \sim 298°K$, field scan = 3300 ± 500 G, frequency = 9.50 GHz.

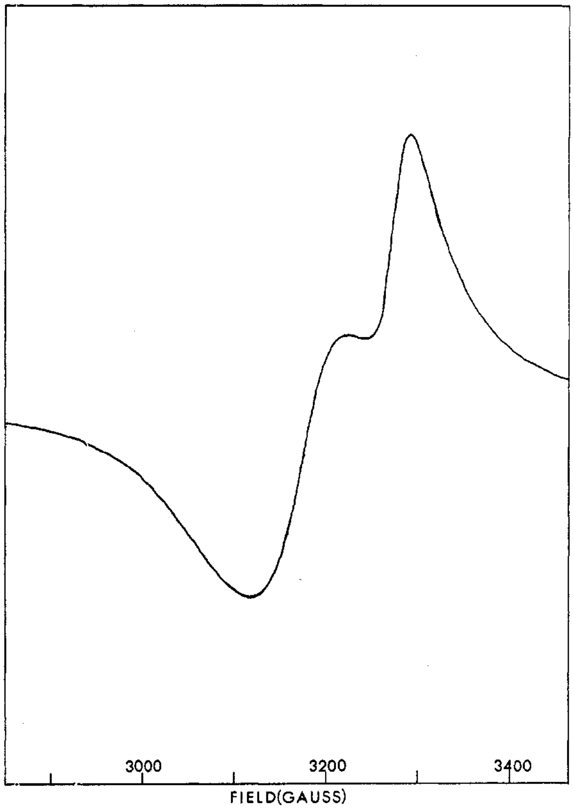

Figure 5.—Epr spectrum of β-bis(8-hydroxyquinolinato)copper(II) (powder), $T = \sim 298°K$, field scan = 3300 ± 500 G, and frequency = 9.49 GHz.

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(8) S. Foner, *Rev. Sci. Instrum.*, **30**, 548 (1959).

(9) J. Lewis and R. G. Wilkins, "Modern Coordination Chemistry," Interscience, London, 1960, p. 403.

for the diamagnetism of the Lucite sample holders. Temperatures were measured with a calibrated, precision germanium resistance thermometer. The X-band, room temperature, electron-paramagnetic-resonance spectra of polycrystalline samples were obtained in the region 1–10,000 G on a Jeolco EPR spectrometer.

Results and Discussion

The magnetic susceptibility of β-Cu(8-OQuin)$_2$ was measured from 3.2 to 77°K. The results are tabulated in Table I and are shown in Figure 3 as a plot of inverse molar susceptibility *vs.* temperature. The susceptibility of the α form was measured down to 4.2°K, and the resulting χ'_m values, which are given in Table II, are very similar to those obtained for the β form with those of the β form being somewhat lower especially at lower temperatures. Although the $1/\chi'_m$ plot intercepts the temperature axis at ∼0°K, there is a slight deviation from the Curie–Weiss law that begins at approximately 7°K. The trend is toward lower susceptibilities than a Curie–Weiss plot would predict.

TABLE I

MAGNETIC SUSCEPTIBILITY DATA FOR β-BIS(8-HYDROXYQUINOLINATO)COPPER(II)

Temperature, °K	$10\chi_m^{cor}$, cgsu	μ_{eff}, BM
3.2	0.9187	1.53
3.4	0.8533	1.52
4.2	0.7730	1.61
4.4	0.7754	1.65
4.5	0.7748	1.66
4.6	0.7741	1.68
4.9	0.7534	1.72
5.2	0.7257	1.73
5.5	0.6854	1.73
5.9	0.6518	1.75
6.4	0.6164	1.77
6.7	0.6476	1.86
7.1	0.5701	1.79
8.1	0.5125	1.82
9.0	0.4616	1.82
9.8	0.4318	1.83
11.1	0.3857	1.85
13.0	0.3335	1.86
15.0	0.2875	1.85
17.6	0.2387	1.83
20.0	0.2052	1.81
23.0	0.1749	1.79
25.0	0.1714	1.85
30.0	0.1438	1.85
34.0	0.1238	1.83
41.0	0.1046	1.85
49.0	0.0885	1.86
56.5	0.0766	1.86
63.0	0.0700	1.87
77.0	0.0570	1.87

TABLE II

MAGNETIC SUSCEPTIBILITY DATA FOR α-BIS(8-HYDROXYQUINOLINATO)COPPER(II)

Temperature, °K	$10\chi_m^{cor}$, cgsu	μ_{eff}, BM
4.2	0.7823	1.62
4.3	0.7834	1.64
5.2	0.7018	1.71
5.7	0.6743	1.75
7.2	0.5806	1.82
9.0	0.4826	1.86
9.7	0.4660	1.90
11.5	0.3975	1.91
14.3	0.3236	1.92
15.4	0.3145	1.96
18.4	0.2529	1.92
24.8	0.1800	1.88
32.0	0.1418	1.90
40.4	0.1140	1.91
49.0	0.0838	1.81
59.0	0.0756	1.88
62.0	0.0663	1.81

Both forms gave epr spectra which exhibited broadened lines centered around 3200 G from which $g_{\parallel}$ and $g_{\perp}$ could be calculated. Each form gave a $\langle g \rangle = 2.10$, while the α from yielded a $g_{\parallel} = 2.16$ and a $g_{\perp} = 2.08$, and the β form yielded a $g_{\parallel} = 2.14$ and a $g_{\perp} = 2.09$. No lines were observed in the half-field region indicative of the $\Delta M_s = \pm 2$ transition. A notable feature of the spectrum of the α form is the flattened $g_{\parallel}$ line, a characteristic associated with interacting species.[10] Using a g value of 2.10, the magnetic susceptibility data for the β form were fitted to the Van Vleck–Bleaney–Bowers equation[11] for two interacting spins of $S = {}^1/_2$. The resulting fit predicts a singlet–triplet separation, $2J = \sim -1$ cm^{-1}. This value is probably not very significant, for limitations in the theoretical model become important for such small interactions. The small exchange coupling for these complexes is primarily due to the relatively large copper–oxygen out-of-plane distance of 2.83 Å for the β form and 3.32 Å for the α form. The related complex bis(pyridine *N*-oxide)copper(II) nitrate has an out-of-plane copper–oxygen distance[12] of 2.44 Å and an exchange energy,[6] $2J \simeq 15$ cm^{-1}. The complex *N,N'*-ethylenebis(salicylideniminato)copper(II) has a corresponding copper–oxygen distance[13] of 2.41 Å and a $2J \simeq 18$ cm^{-1}.

Although there is magnetic coupling in α- and β-Cu(8-OQuin)$_2$, as is evidenced by their epr spectra, the magnitude of the interaction is very small. In order to more precisely determine the nature of the ground state in these compounds, it will be necessary to carry out susceptibility measurements at even lower temperatures. These low temperatures will necessitate a careful consideration of the field dependence of susceptibility. However, the data presented here are important for they indicate that out-of-plane copper–oxygen distances of 2.83 Å, or greater, are too long to transmit significant exchange coupling. It now becomes important to examine the magnetic properties of parallel-planar copper(II) dimers in which the out-of-plane copper–oxygen distances fall between 2.4 and 2.8 Å.

Acknowledgments.—This research was supported by the National Science Foundation under Grant No. GP-22887, and by the Materials Research Center of the University of North Carolina through Contract DAHC 15-67-CO223 with the Advanced Research Projects Agency.

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