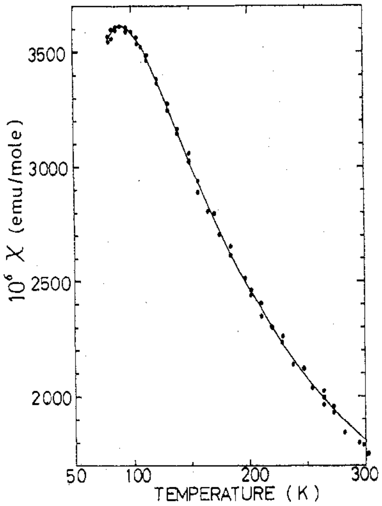

Figure 1. Calculated susceptibility of the oligomer complex $[FeS_4C_4(CF_3)_4]_2$ compared with the experimental data by Dance. The calculation is made with the values of the parameters $J = -210\ cm^{-1}$, $J' = -53\ cm^{-1}$, and $\chi_{const} = -500 \times 10^{-6}$ cgsu.

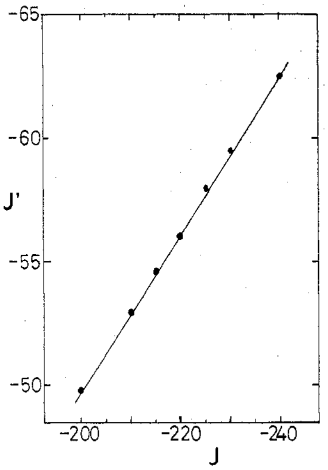

Figure 2. The relation of J and J' which reproduces the observation. The numerical values are in units of cm^{-1}.

treatment. The coefficient J' of the biquadratic exchange interaction is related to the coefficient K_3 of the higher order spin coupling which depends strongly on the overlap integrals between wave functions of electrons participating in the exchange interaction.[3] The unusually large relative value of J' is not so unreasonable in the present oligomeric complex as considerable amounts of the overlap between wave functions may be expected in this case.

In the present fitting procedures, the parameter J' seems to change linearly with the parameter J as shown in Figure 2. Since the strength of the biquadratic exchange interaction may usually be estimated as 20–30% at most of that of the Heisenberg exchange,[5] the relation of J and J' shown in Figure 2 may not be extended so far. As we have pointed out in the previous studies,[6] the biquadratic exchange interaction may be important for binuclear complex compounds. For tri- or quadrinuclear complex compounds, generally the other types of the higher order spin couplings may appear.[7,8] In the present studies, however, the origin of the biquadratic exchange interaction has been elucidated in relation to the general exchange mechanism of many-electron system.

Registry No. $[FeS_4C_4C(CF_3)_4]_2$, 41959-83-5.

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Lewis Acid Properties of Copper(II) in Cu(II)-N_2O_2-Chelate Complexes

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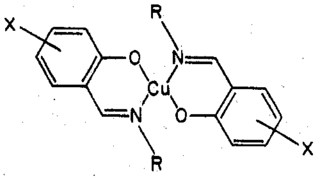
Copper(II) readily forms neutral bis complexes CuL_2 with Schiff bases prepared from salicylaldehyde and aliphatic (see I) or aromatic amines (see II). Kinetic studies of the metal[1] and ligand exchange[2] behavior of CuL_2 in organic solvents have led to the conclusion that substituent effects, as introduced by variation of X and Y, are kinetically operative only when changes in electron density at donor *oxygen* are involved. Variation of Y and, hence, changes of electron density at donor *nitrogen* seem to contribute kinetically only via corresponding changes at donor oxygen.[1b] The interesting questions are, therefore, in which way X and Y affect the electron density of O and N and in which way the electron density at the central copper is involved.



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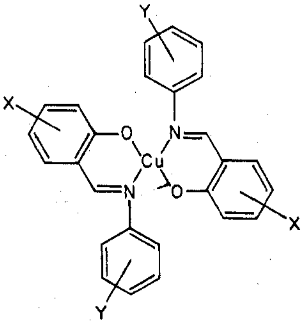

II

In noncoordinating solvents the copper in CuL_2 is four-coordinated,[3] the coordination geometry varying between square planar and pseudotetrahedral,[4] depending on the nature of X and R. Coordinating solvents like pyridine cause spectral changes due to the formation of five- or six-coordinated copper(II) species.[5] Therefore, the equilibrium constant K of this Lewis acid–base reaction (as described by eq 1) is a

$$CuL_2 + x\,py \overset{K}{\rightleftharpoons} CuL_2{\cdot}x\,py \qquad (x = 1, 2) \qquad (1)$$

quantitative measure of the electron density available at the d_{z^2} orbital of Cu(II). On the basis of spectrophotometric studies, we report the effect of the parameters X, Y, and R on K.

Experimental Section

The bis(salicylaldiminato)copper(II) complexes CuL_2 were prepared by standard procedures.[3] The results of elemental analysis were in good agreement with theoretical data. Analytical grade toluene and pyridine (E. Merck, Darmstadt) were used as solvents without further purification. The absorption spectra were recorded with a Zeiss DMR 22 spectrometer at 400–800 nm in thermostated quartz cells of 2- and 10-cm path length. The temperature inside the cells was controlled with a thermocouple.

In each case 20 solutions of the complex in toluene were prepared ($[CuL_2]$ = constant; [py] = 0–12.4 M) and their spectra recorded at 298, 313, and 333 K. For all complexes and temperatures an

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Table I. Equilibrium Constants and Thermodynamic Data for the Adduct Formation of Complexes I and II with Pyridine and Other Donor Molecules

	Complex						
No.	Type	X	R(I), Y(II)	Donor	K_{298}, M^{-1}	$-\Delta H^\circ_{298}$, kJ mol^{-1}	$-\Delta S^\circ_{298}$, J K^{-1} mol^{-1}
1	I	5-OMe	Et	py	0.32 ± 0.026	13 ± 2.0	53 ± 7
2	I	5-Me	Et	py	0.36 ± 0.024	8.0 ± 1.2	35 ± 4
3	I	5-H	Et	py	0.54 ± 0.023	9.2 ± 2.1	36 ± 7
4	I	5-F	Et	py	0.61 ± 0.018	11.1 ± 0.5	41 ± 2
5	I	5-Cl	Et	py	0.97 ± 0.037	17.9 ± 0.5	60 ± 2
6	I	5-Br	Et	py	1.09 ± 0.060	20.7 ± 0.5	69 ± 2
7	I	5-I	Et	py	1.13 ± 0.025	20.7 ± 1.6	68 ± 5
8	I	5-NO_2	Et	py	5.4 ± 0.40	23.3 ± 3.6	64 ± 12
9	I	H	*i*-Pr	py	0.21 ± 0.014	−0.3 ± 3.1	12 ± 10
10	I	H	*t*-Bu	py	0.31 ± 0.089		
11	I	H	*n*-Pr	py	0.51 ± 0.015	8.7 ± 0.6	35 ± 2
12	I	H	*i*-Bu	py	0.36 ± 0.015	5.6 ± 1.3	27 ± 5
13	I	H	*neo*-Pe	py	0.17 ± 0.038	0.4 ± 9.7	16 ± 33
14	II	H	4-Me	py	1.29 ± 0.034	13.6 ± 1.0	43 ± 3
15	II	H	4-H	py	1.75 ± 0.029	19.6 ± 0.6	61 ± 2
16	II	H	4-Cl	py	2.38 ± 0.039	8.3 ± 1.9	21 ± 6
17	II	H	4-I	py	3.07 ± 0.051	19.8 ± 0.6	57 ± 2
18	II	H	4-CN	py	7.8 ± 0.26	23.3 ± 3.8	61 ± 13
19	II	H	2,6-Cl_2	py	2.18 ± 0.041	19.6 ± 1.0	59 ± 3
20	II	H	2,4,6-Me_3	py	1.27 ± 0.036	25.1 ± 1.5	82 ± 5
21	I	5-I	Et	2-Me(py)	0.24 ± 0.091		
22	I	5-I	Et	4-Me(py)	2.4 ± 0.13	19.7 ± 3.6	59 ± 12
23	I	5-I	Et	4-CN(py)	0.47 ± 0.021		
24	I	5-I	Et	2,6-Me_2(py)	0.03 ± 0.02		
25	I	5-I	Et	Quinoline	<0.03		

isosbestic point between 600 and 700 nm was obtained. The absorbance A at a wavelength with maximum changes in optical density was selected for calculating the equilibrium constant K. The observed values for A were fitted to eq 2 with a computer program using the

$$K = \frac{A - A_A}{A_B - A}\,\frac{1}{[\mathrm{py}]} = \frac{[\mathrm{CuL_2{\cdot}py}]}{[\mathrm{CuL_2}][\mathrm{py}]} \qquad (2)$$

least-squares procedure to obtain the best values for K, A_A (=absorbance of CuL_2 in toluene) and A_B (=absorbance of CuL_2·py). The enthalpy and entropy of reaction 1 were determined from ln K = f(1/T).

Results and Discussion

The spectral changes observed are consistent with the formation of 1:1 adducts between CuL_2 and pyridine (x = 1 in eq 1): (i) an isosbestic point is obtained for the whole range of pyridine concentrations, (ii) the calculated equilibrium constants are independent of the wavelength ranging from 400 to 800 nm, and (iii) plotting of log $[(A - A_A)/(A_B - A)]$ vs. log [py] according to eq 2 results in straight lines with slope 1.

The values of K obtained for the adduct formation of complexes I and II and the enthalpy and entropy data are compiled in Table I.

The comparison with β-diketonatocopper(II) complexes reveals that the acidic character of the copper in complexes CuL_2 of types I and II is clearly reduced. For Cu$(acac)_2$[6] the equilibrium constant for adduct formation with pyridine is 75.2 in dichloromethane[7a] and 8.7 in benzene.[7b]

The general behavior, however, of only one pyridine molecule being coordinated is the same. In this respect the copper(II) complexes are different from their nickel(II) analogues,[5] which in general are six-coordinated in pyridine as solvent. This difference is probably due to the additional electron of the d^9 system.

As shown in Table I, there is a marked influence of substituents X (in the 5-position of the salicylaldehyde ring) and substituents Y (in the 4-position of the aniline ring) on the equilibrium constant K, whereas variations in the alkyl group R are of minor significance only.

For the sequence Cu$(acac)_2$–Cu$(tfac)_2$[6]–Cu$(hfac)_2$[6] the acidic character of the copper is found to increase as indicated by increasing equilibrium constants K.[7c] The electron-withdrawing CF_3 groups obviously facilitate adduct formation. As a consequence, with Cu$(hfac)_2$ even the addition of a second pyridine molecule is observed.

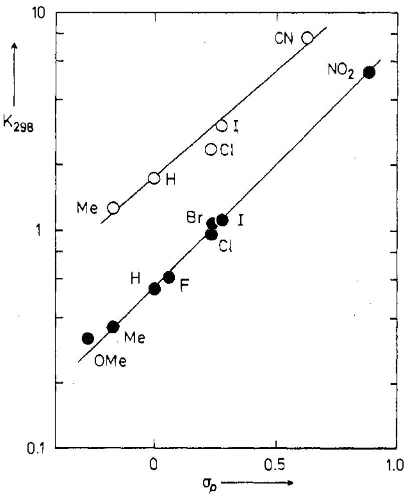

Figure 1. Hammett plots for the equilibrium constants K: ○, II with X = H, variation of 4-Y; ●, I with R = Et, variation of 5-X.

Electron-withdrawing and electron-releasing properties of substituents Y at the aniline ring affect primarily the electron density at the donor nitrogen in II. The variations in K observed with varying Y clearly prove that electron density is obviously transferred between nitrogen and copper(II), i.e., the d_{z^2} orbital of Cu(II), which is presumably involved in the acid–base reaction 1. Plotting of log K vs. Hammett's substituent constants σ_p[9] gives a straight line with slope ρ(N) = 0.97 (see Figure 1). The electronic properties of substituents X in the 5-position of the salicylaldehyde ring affect, in principle, both the donor oxygen and the donor nitrogen. Which of these effects dominates should be clearly decided by the results of Hammett plots based alternatively on meta and para substituent constants. As shown in Figure 1, the latter (σ_p) result in a straight line with slope ρ(O) = 1.19, whereas for the former (σ_m), scattering of the data is observed.

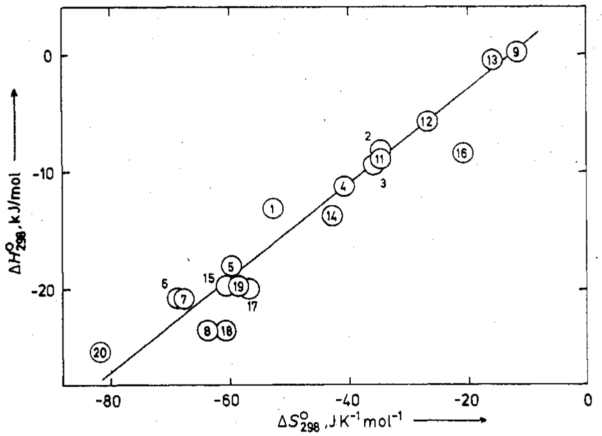

Figure 2. Linear free energy plot. The numbers represent the systems given in Table I.

One learns, therefore, that substituents X induce transfer of electron density between oxygen and copper.

The fact that both X and Y substituent effects can be rationalized on the basis of *positive* values for ρ is consistent with the interpretation of electron deficiency at the d_{z^2} orbital of copper facilitating the adduct formation with donor molecules like pyridine.

Spectroscopic studies indicate the contribution of some π bonding to the copper–oxygen interaction, whereas for the copper–nitrogen bond no π bonding can be inferred.[8] The interesting fact that Hammett plots for both the X and Y dependencies result in nearly the same positive value for the reaction constant ρ leads to the conclusion, therefore, that charge transfer between the donor atoms and the central copper ion occurs via an inductive mechanism only.

Introduction of substituents Y in the 2- and 6-positions of the aniline ring—expected to build up considerable steric hindrance for adduct formation—influences K only slightly (see Table I). Branching of the alkyl groups R at the α- and β-carbon atoms decreases K (for R = *t*-Bu the observed spectral changes are very small and consequently the error for the corresponding K value is high).

The variation of K observed upon introduction of substituents in the pyridine molecule is not unexpected (see Table I). Electron-withdrawing (-releasing) groups decrease (increase) K, and steric hindrance (CH_3 in the 2-position) makes the addition of the base more difficult. With 2,6-lutidine and quinoline practically no adduct formation does occur, although small spectral changes are observed. The enthalpy and entropy data shown in Table I are negative, as expected for an addition reaction like (1). The addition of pyridine to the various complexes is, however, neither an isoenthalpic nor an isoentropic process. The linear free energy plot of ΔH°_{298} vs. ΔS°_{298} leads to a satisfying linear relationship with a slope of +0.40 (see Figure 2). This would mean that the more exothermic the acid–base reaction is, the less mobile the coordinated pyridine becomes.

In summary, the study of equilibrium 1 leads to the following conclusions, mainly based on Hammett plots: (i) In complexes CuL_2 substituents X transfer electron density to the copper through oxygen and substituents Y through nitrogen. (ii) This transfer of electron density through oxygen (X) and through nitrogen (Y) is practically of the same size for a given set of substituents; i.e., $\rho(O) \approx \rho(N) \approx +1$ (see Figure 1). (iii) Adduct formation according to (1) is mainly determined by electronic factors, whereas steric effects play a minor role only.

One has to consider what bearing these thermodynamic arguments have on the kinetic findings mentioned earlier. These stem from an investigation of the isotopic metal[1a,b] (in chloroform and dichloromethane) and ligand exchange[2] (in toluene) of complexes I and II, substituents X and Y and the aliphatic group R (in I) being the parameters. Evaluation of the kinetic data led to the following results: (i) The rate of exchange is strongly governed by the electron density at the donor oxygen.[1a] (ii) Hammett plots (based on rate constants) yield linear relationships for complexes with substituents X in the 5- and 4-positions: the reaction constant $\rho(O)$ however is *negative*, ranging from -1.0[1b] to -1.5.[1a] (iii) Variation of Y in complexes II leads to a rather small reaction constant $\rho(N) = -0.35$.[1b] (iv) Introduction of substituents Y in the 2- and 6-positions of the aniline ring decreases the rate by a factor of up to 400.[1b]

These findings led us to the conclusion that exchange is initiated by the attack of residual water at the Cu–O bond and that the cleavage of this bond is rate determining.[1,2] The results of the present thermodynamic study support this interpretation in the sense that on the basis of the ρ values derived from K, any rate-determining attack at the copper can be excluded.

The question of how substituents Y affect the electron density at the donor oxygen—a neighboring effect through copper or conjugation through an aromatic system—cannot be answered conclusively.

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Registry No. **1**·py, 66069-96-3; **2**·py, 66069-95-2; **3**·py, 66069-94-1; **4**·py, 66069-93-0; **5**·py, 66069-92-9; **6**·py, 66069-91-8; **7**·py, 66069-90-7; **8**·py, 66069-89-4; **9**·py, 66069-88-3; **10**·py, 66069-87-2; **11**·py, 66070-07-3; **12**·py, 66070-06-2; **13**·py, 66070-05-1; **14**·py, 66070-04-0; **15**·py, 14837-79-7; **16**·py, 66070-03-9; **17**·py, 66070-02-8; **18**·py, 66070-01-7; **19**·py, 66102-26-9; **20**·py, 66102-25-8; **21**·2-Me(py), 66070-00-6; **22**·4-Me(py), 66069-99-6; **23**·4-CN(py), 66069-98-5; **24**·2,6-Me_2(py), 66102-27-0; **25**·quinoline, 66069-97-4.

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Formation and Decomposition of Thiosulfate in the Ferrous Sulfide–Sulfur Dioxide Reaction[1]

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In a recent series of experiments we have confirmed the formation of thiosulfuric acid in the aqueous oxidation of FeS by SO_2 and shown that the acid decomposition of thiosulfate