

Studies on Intermolecular Interactions of Metal Chelate Complexes. VI. On the Selfredox Reaction of Copper(II) Dithiophosphinates

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Summary

The kinetics of the inner selfredox reaction of $\text{Cu}(\text{dtph})_2$ (dtph = dithiophosphinate) was studied by e.p.r. The reaction is second order in $\text{Cu}(\text{dtph})_2$ with effective rate constant $5.5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (at 300 K); the plot of $\log k_{\text{eff}}/(1/T)$ is not of Arrhenius type, suggesting that k_{eff} depends on the equilibrium constant for the formation of a precursor between two molecules of $\text{Cu}(\text{dtph})_2$. On the other hand, the differences in a_0 and a_{av} ($a_0 < a_{\text{av}}$) extracted from e.p.r. spectra in solution and frozen solution or magnetically dilute samples suggest that $\text{Cu}(\text{dtph})_2$ is associated in solution, whereas in the other two forms it is a monomer. The observed instability of $\text{Cu}(\text{dtph})_2$ towards inner selfredox reaction is compared to that of other sulphur-containing $\text{Cu}(\text{II})$ complexes and discussed in terms of the relatively low redox potential of the ligand.

Introduction

Previous studies⁽¹⁾ on dithiophosphinate complexes $\text{M}(\text{dtph})_2$ ($\text{dtph} = \text{R}_2\text{PS}_2$) have suggested that $\text{Cu}(\text{dtph})_2$ does not exist, due to the reduction of $\text{Cu}(\text{II})$ to $\text{Cu}(\text{I})$ by the ligands. This was based on analytical data. Later e.p.r. data^(2–6) proved the existence of $\text{Cu}(\text{dtph})_2$, though unstable with respect to reduction of $\text{Cu}(\text{II})$ to $\text{Cu}(\text{I})$.

In general, $\text{Cu}(\text{II})$ dithiophosphinates have been shown⁽⁷⁾ to exist in solution and in the molten state, and to reduce to $\text{Cu}(\text{I})$ in the solid state. Only the *o*-cresyl derivative was obtained as $\text{Cu}(\text{II})$ complex in solution, and in the molten and solid states. The reduction reaction is reversible, and was described as an inner selfredox reaction. The available data suggest⁽⁷⁾ that this reaction proceeds as a result of association between two neighbouring molecules during the crystallization. Since the reaction takes place in super-saturated solutions it was not possible to follow its kinetics. However, this is not true of dithiophosphinato-complexes and they were used to elucidate details of the selfredox reaction.

Results and Discussion

Typical e.p.r. spectra of copper(II) bis(dithiophosphinate) complexes dissolved in toluene at 300 and 77 K are shown in Figure 1. A powder spectrum typical of $\text{Cu}(\text{dtph})_2$ magnetically diluted in the corresponding $\text{Ni}(\text{II})$ host lattice is shown in Figure 2.

Superhyperfine (shf) splitting due to two ^{31}P nuclei is clearly observed at 300 K (Fig. 1a), whereas it is not well resolved at 77 K (Fig. 1b), which might be attributed to the broadening of the shf lines. On the other hand, the powder e.p.r. spectrum of magnetically dilute sample exhibits well resolved shf splitting.

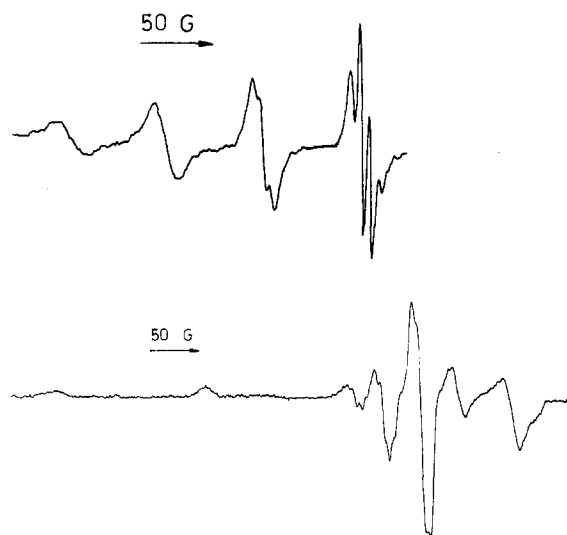
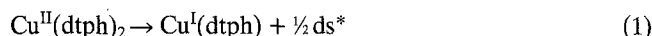


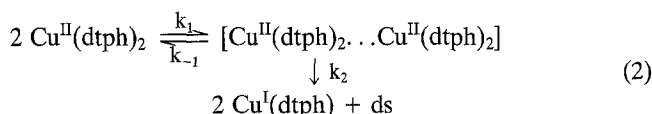
Figure 1. E.p.r. spectra typical for copper(II) bis(dithiophosphinate) complexes dissolved in toluene: a at 300 K, b at 77 K.

The e.p.r. parameters calculated from these spectra, as well as those available in the literature, are shown in Table 1. As can be seen the influence of the remote ligand substituents is negligible and is not greater than the order of experimental error. This suggests that the distribution of the unpaired electron density in $\text{Cu}(\text{dtph})_2$ is determined mainly by the S atoms, which are the most powerful donors in the ligand molecule.

The data of a_0 show some differences compared to a_{av} calculated from the anisotropic e.p.r. spectra of $\text{Cu}(\text{dtph})_2$ (Table 1). These differences are significant compared to experimental error and may be explicable in terms of specific interactions. One possibility is the formation in solution of an adduct between $\text{Cu}(\text{dtph})_2$ and ds formed by the reaction (1)



However, the e.p.r. parameters remain unchanged between 77 and 300 K, when ds is added to the solution. In addition it has been shown⁽⁸⁾ that adduct formation leads to the $g_{\text{av}} < g_0$ and $a_{\text{av}} > a_0$, so this also suggests that adduct formation does not occur. Another explanation could be an association of molecules $[\text{Cu}(\text{dtph})_2 \dots \text{Cu}(\text{dtph})_2]$ as an intermediate product in the selfredox reaction (2) of $\text{Cu}(\text{dtph})_2$.



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* ds – corresponding disulphide.

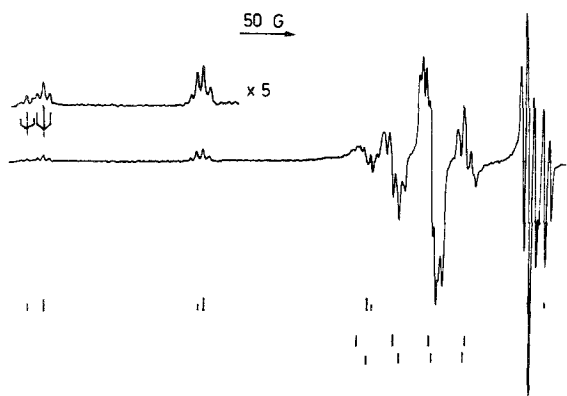


Figure 2. E.p.r. spectrum typical for powders of magnetically dilute copper(II) bis(dithiophosphinates) in the corresponding Ni^{II} host lattice.

This possibility is supported by the kinetics of the selfredox reaction, which is of second order (Fig. 3) with respect to Cu^{II}(dtp)₂. The effective rate constant at 300 K is $k_{\text{eff}} = 5.5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The plot of $\log k_{\text{eff}}(1/T)$ (Fig. 4) was not of Arrhenius type, suggesting that k_{eff} is a function not only of k_2 but probably also depends on k_1/k_{-1} .

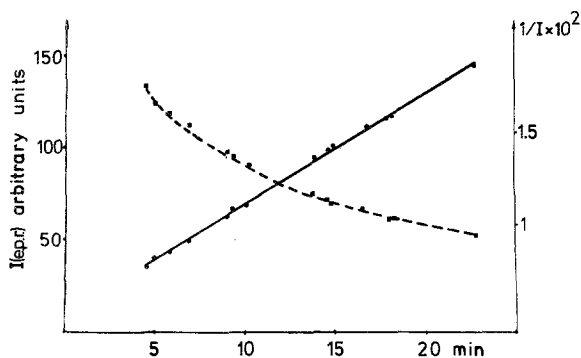


Figure 3. Dependence of the intensity of the e.p.r. spectra of copper(II) bis(dithiophosphinates) (I , in arbitrary units relative to DPPH) (dashed line) and of $1/I$ on time (solid line).

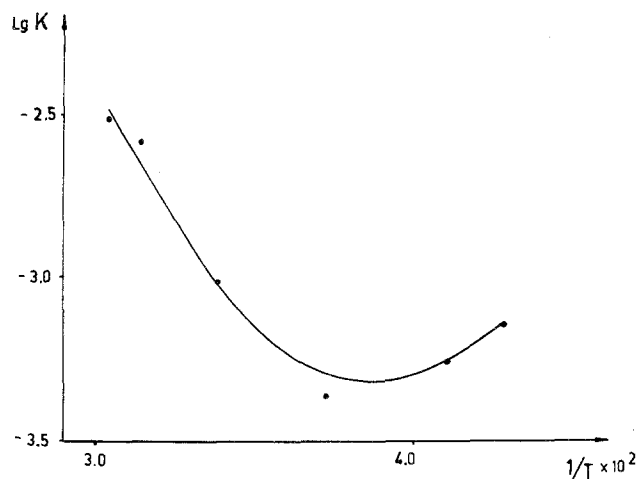


Figure 4. Plot of $\log k_{\text{eff}}$ versus $1/T$ for copper(II) bis(dithiophosphinate) complexes.

Since at lower temperatures equilibrium (2) should be shifted to the right, it was expected that decreasing the temperature from 300 to 77 K should increase the formation of Cu^I(dtp). In fact, freezing the Cu^{II}(dtp)₂ solution for a short time at 77 K followed by defreezing causes a 30–40% decrease of Cu^{II}(dtp)₂ concentration compared to that of similar sample kept at room temperature. The e.p.r. spectrum of Cu^{II}(dtp)₂ in solution at room temperature is affected by equilibrium (2), whereas at 77 K and in magnetically dilute samples it corresponds to the isolated monomeric form. The above results are consistent with the fact that Cu(dtp)₂ ($R = 3,4\text{-Me}_2\text{C}_6\text{H}_3$ or $2,5\text{-Me}_2\text{C}_6\text{H}_3$) are stable in solution and in the solid state⁽⁹⁾. The bulky substituents prevent association and reaction (2) cannot proceed.

Once obtained in solid state, Cu^I(dtp) is not oxidized back to Cu^{II}(dtp)₂ and remains insoluble in the usual organic solvents. When heated, Cu^I(dtp) decomposes without melting. The corresponding disulphides possess well defined melting points 56–7°C ($R = \text{Et}$), 79–80°C ($R = \text{Pr}^n$) and 145°C ($R = \text{Ph}$), respectively^(1, 10).

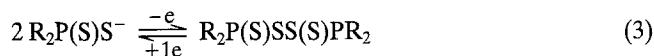
The observed instability of Cu^{II}(dtp)₂ complexes compared to the corresponding Cu(dtp)₂ and copper(II) bis(dithiocarba-

Table 1. E.p.r. parameters of Cu(S₂PR₂)₂ complexes.

Complex	g_0 (± 0.001)	a_0^{Cu} ($\pm 1 \text{ G}$)	a_0^{P} ($\pm 0.5 \text{ G}$)	g_{\parallel} (± 0.001)	g_{\perp} (± 0.001)	a_{\parallel} ($\pm 1 \text{ G}$)	a_{\perp} ($\pm 1 \text{ G}$)	a^{P} ($\pm 0.5 \text{ G}$)	g_{av}	a_{av}	a_{an}	Ref.
[(C ₂ H ₅) ₂ PS] ₂ Cu	2.054	67.1	5.1									6
[(C ₂ H ₅) ₂ PS] ₂ Cu/Ni				2.110	2.029	165 ^{a)} 154 ^{b)}	37	5.5	2.056	76	39	7, 8
[(C ₂ H ₅) ₂ PS] ₂ Cu	2.054	70	5.0	2.110	2.029	158 ^{a)}	37	6	2.056	76	39	8
[(C ₂ H ₅) ₂ PS] ₂ Cu	2.055	69	5.7	2.104	2.029	158	39		2.054	79		t.w. ^{c)}
[(C ₂ H ₅) ₂ PS] ₂ Cu/Ni				2.104	2.027	164 ^{a)}	33	5.7	2.053	76		t.w.
[(n-C ₃ H ₇) ₂ PS] ₂ Cu	2.054	69	5.7	2.101	2.024	159	38		2.048	78	40	9
[(n-C ₃ H ₇) ₂ PS] ₂ Cu	2.056	70	5.7	2.101	2.028	153	38		2.052	76	39	t.w.
[(n-C ₃ H ₇) ₂ PS] ₂ Cu/Ni				2.098	2.027	162 ^{a)} 150 ^{b)}	34	5.7	2.049	75		t.w.
[(C ₆ H ₅) ₂ PS] ₂ Cu	2.053	66.1	5.6									6
[(C ₆ H ₅) ₂ PS] ₂ Cu			6.6									10
[(C ₆ H ₅) ₂ PS] ₂ Cu	2.054	70	6.7	2.100	2.028	163 ^{a)} 154 ^{b)}	38	5.7	2.052	80	41	t.w.
[(C ₆ H ₅) ₂ PS] ₂ Cu/Ni				2.100	2.029	159 ^{a)} 151 ^{b)}	35	5.7	2.053	76	41	t.w.

^{a)} Cu⁶⁵. ^{b)} Cu⁶⁴. ^{c)} t.w. – this work.

mates) may be due to the relatively low redox potentials of the ligands. The formal redox potential of the reaction (3) is



0.11 V ($R = n\text{-C}_3\text{H}_7$)⁽¹¹⁾, whereas for dithiophosphates $E_0 = 0.25$ ⁽¹²⁾ and for dithiocarbamates $E_0 = 0.33$ V⁽¹³⁾. The stability towards selfredox reactions increases in the order of the redox potentials: dtph < dtp < dtc.

Experimental

Na(dtph) (dtph = R_2PS_2 , $R = C_2H_5$, $n\text{-C}_3H_7$ or C_6H_5) were synthesized by methods described previously⁽¹⁰⁾.

Copper(II) bis(dithiophosphinate) complexes were prepared by extraction of the aqueous solutions of $CuCl_2$ and the corresponding sodium dithiophosphinates with a non-polar organic solvent and were studied immediately after preparation.

In order to dope $Cu^{II}(dtph)_2$, the corresponding $Ni^{II}(dtph)_2$ were synthesized analogously.

Magnetically dilute $Cu^{II}(dtph)_2$ samples were obtained by exchange of approximately 1% of the Ni^{II} complex with Cu^{II} complex.

Disulphides of dithiophosphinates, $ds = [R_2P(S)SS(S)Pr_2]$, were obtained by adding H_2O_2 to an aqueous solution of Na

dtph. E.p.r. spectra were recorded on a 3 BS-X spectrometer using 100 kHz modulation of the magnetic field. The magnetic field was calibrated with Mn^{2+} in MgO . The g values were determined relative to DPPH.

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New Metal-Chelate Complexes Derived from the Condensation Product of Biacetylmonoxime and *N,N*-Dimethylglycine Hydrazide Hydrochloride (Girard's D Reagent)

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Summary

The reactions between the condensation product of biacetylmonoxime and *N,N*-dimethylglycine hydrazide hydrochloride, [BMGD]Cl, and the hydrated Ni^{II} , Cu^{II} , Cd^{II} , Hg^{II} and $U^{VI}O_2$ salts give chelate complexes of types $[M(BMGD)Cl_2]Cl$ ($M = Cd^{II}$ or Hg^{II}), $[Cu(BMGD)_2Br_2]Cl_2$ and $[M(BMGD-H)_2 \cdot (H_2O)_2]Cl_2 \cdot YH_2O$ ($M = Ni^{II}$, Cu^{II} or $U^{VI}O_2$). Elemental analyses, magnetic measurements and spectra (i.r., visible, n.m.r.) have been used to characterize the complexes. I.r. spectral data show that the ligand is monodentate, coordinating via the azomethine group of the hydrazone, or bidentate, coordinating through the azomethine and the carbonyl oxygen groups. The enolization of the carbonyl oxygen involves the NH rather than the CH_2 group. The stereochemistry of the Ni^{II} and Cu^{II} complexes is discussed.

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Introduction

Previous papers⁽¹⁻⁵⁾ from this laboratory have concerned the preparation and characterization of some hydrazone-oxime complexes of some transition metal ions. Here we report the preparation and characterization of metal complexes of [BMGD]Cl, prepared from biacetylmonoxime and *N,N*-dimethylglycine hydrazide hydrochloride. The stereochemistry of the complexes isolated was determined by magnetic and spectral studies.

Experimental

All the chemicals were reagent grade (BDH) except *N,N*-dimethylglycine hydrazide hydrochloride (Girard's D reagent) which was purchased from Fluka A. G. and used as supplied. The ligand (I) was prepared by the usual method⁽²⁾ and had m.p., 272°C.