Electron Spin Resonance Study of Adduct Formation by Bis(trifluoroacetylacetonato)copper(II) with Phosphorus Donor Ligands

F. LEH and K. M. CHAN*

Air Pollution Research Center, University of California, Riverside, California 92502, U.S.A.
* *California State University, Long Beach, California 90840, U.S.A.*

(Received September 6, 1971)

The study of the ESR spectra parameters of bis(trifluoroacetylacetonato)copper(II)-phosphorus complexes in chloroform solution at room temperature and 77°K shows that the g and hyperfine tensors change with the formation of 1: 1 adduct. Such effect is more clearly exhibited by the parameters $A_{\parallel}$ and $g_{\parallel}$. A correlation is obtained between the spectral data and the basicity of the tertiary phosphine ligands.

High spin divalent transition metal ions usually have strong tendency to form compounds having a coordination number greater than four.[1] For example, the axial ligation of bis(acetylacetonato)copper(II) forms 1: 1 adduct with heterocyclic bases.[2,3] However, such adduct formation depends on the relative electron withdrawing power of the β-diketones.[4] Successive trifluoromethylation of the acetylacetones will increase their affinity for the copper atom for axial ligation, which has been demonstrated by the formation of 1: 1 and/or 1: 2 addition complexes with donor solvent and nitrogen containing chelates by bis(trifluoroacetylacetonato)copper(II)[5] and bis(hexafluoroacetylacetonato)-copper(II).[6,7]

The preparation of the above complexes of σ-type nitrogen containing ligands are well documented, but not for π-type bases. This is primarily due to the fact that copper(II) salts react with tertiary phosphine and are reduced to copper(I) compounds.[8-10] Only recently the preparation of 1: 1 adduct of bis(hexafluoroacetylacetonato)copper(II) with triphenylphosphine was reported.[11] This paper describes our work in ESR study of 1: 1 adducts of bis(trifluoroacetylacetonato)copper(II) with tertiary phosphines.

Solvent Effect on Copper Complexes

Antosik *et al.*[12] analysed the effect of the solvent on axial ligations. Based on the ESR spectra of several square planar cupric β-ketoenolates, they concluded that the axial ligation arose from the two-axial dipoles acting on the two axes perpendicular to the plane of cupric complexes. First-order perturbation theory was used to obtain the relationships between the spin-Hamiltonian parameters for the 'isolated' complexes with those for the perturbed complexes. Greater values of the parallel components of the g tensors and numerically smaller values of the parallel components of the hyperfine tensor for the chloroform complexes than that of the corresponding components in the 'isolated' cupric chelates were predicted.

A systematic investigation of the ESR parameter $\langle A\rangle$ of bis(t-butylacetoacetato)copper(II) in different organic solvents such as cyclohexane, carbon tetrachloride, benzene, chloroform, pyridine–cyclohexane mixture, was carried out by Libutti, Wayland, and Garito.[13] Basic solvents, *e.g.* pyridine, caused a large decrease in $\langle A\rangle$ values and an increase in $\langle A\rangle$ values occurred if less coordinating solvents were used. Another study with ESR spectra of bis(acetylacetonato)-copper(II) in various solvents was reported by Adato and Eliezer,[7] and showed that the anisotropy of the nuclear hyperfine interaction tensor varied with different solvents. Such effect was claimed to be better obtained from the hyperfine splitting parameter $A_{\perp}$.

Experimental

Dark green bis(trifluoroacetylacetonato)copper(II)-phosphorus complexes, $Cu(tfac)_2 \cdot PR_3$ (where $PR_3=(n\text{-}Bu)_3P$, Et_3P, Ph_3P, $PhPMe_2$, Ph_2PMe, $(PhO)_3P$) were prepared by mixing 1: 1 ratio of bis(trifluoroacetylacetonato)copper-(II) with phosphine in chloroform solution under nitrogen. Bis(trifluoroacetylacetonato)copper(II)-phosphorus complexes are quite stable in vacuum at 0°C, but decompose rapidly when heated over 50°C.

ESR spectra were recorded with a Varian V-4502 EPR spectrometer equipped with a 100-kHz field modulation and control unit (Model V-4560). The g values were measured by comparison with the free radical standard diphenylpicryhydrazyl (DPPH) for which the g_0 value was accurately known to be 2.0036.

Results and Discussion

In chloroform solution, bis(trifluoroacetylacetonato)copper(II)-phosphorus complexes, $Cu(tfac)_2 \cdot PR_3$ ($PR_3=Et_3P$, $(n\text{-}Bu)_3P$, Ph_2PMe, $PhPMe_2$) exhibit the

---

[1] D. P. Graddon, *Coord. Chem. Rev.*, **4**, 1 (1969).
[2] D. P. Graddon and E. C. Watton, *J. Inorg. Nucl. Chem.*, **21**, 49 (1961).
[3] R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, **1963**, 5399.
[4] W. Partenheimer and R. S. Drago, *Inorg. Chem.*, **9**, 47 (1970).
[5] R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, **1963**, 5885.
[6] D. E. Fenton, R. S. Nyholm, and M. R. Truter, *J. Chem. Soc., A*, **1971**, 1577.
[7] I. Adato and I. Eliezer, *J. Chem. Phys.*, **54**, 1472 (1971).
[8] W.E. Hatfield and R. Whyman, "Transition Metal Chemistry", ed. R. L. Calvin, Dekker, New York (1969), pp. 5, 47.
[9] F. G. Moss and P. H. Op Het Veld, *J. Inorg. Nucl. Chem.*, **32**, 3225 (1970).
[10] W. A. Anderson, A. J. Carty, G. J. Palenik, and G. Schreiber, *Can. J. Chem.*, **49**, 761 (1971).
[11] M. Baird and R. A. Zaronka, *Chem. Commun.*, **1971**, 448.
[12] S. Antosik, N. M. D. Brown, A. A. McConnell, and A. L. Porte, *J. Chem. Soc., A*, **1969**, 545.
[13] B. L. Libutti, B. B. Wayland, and A. F. Garito, *Inorg. Chem.*, **8**, 1510 (1969).

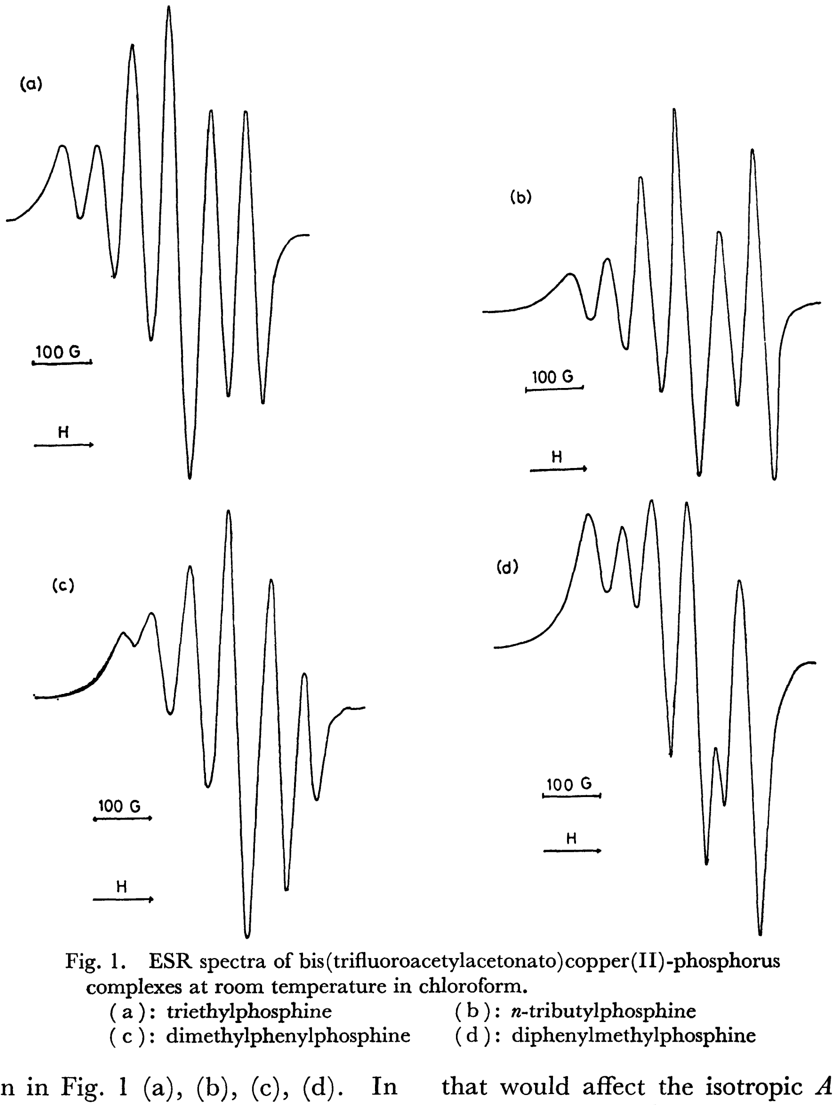


Fig. 1. ESR spectra of bis(trifluoroacetylacetonato)copper(II)-phosphorus complexes at room temperature in chloroform.
(a): triethylphosphine (b): *n*-tributylphosphine
(c): dimethylphenylphosphine (d): diphenylmethylphosphine

ESR spectra as shown in Fig. 1 (a), (b), (c), (d). In a polycrystalline sample, all molecules are assumed to be in an identical environment, and their microcrystalline axes randomly oriented. In a frozen solution spectra (Fig. 2), it is possible to obtain $g_{\parallel}$ and $A_{\parallel}$, and from these values we calculated $g_{\perp}$ and $A_{\perp}$ using the approximate equations $\langle g\rangle = g_{\parallel}/3 + 2g_{\perp}/3$ and $\langle A\rangle = A_{\parallel}/3 + 2A_{\perp}/3$, where $\langle A\rangle$ and $\langle g\rangle$ are obtained in solution assuming that the freezing of the solvent does not change the local crystal field in a manner that would affect the isotropic A and g values.

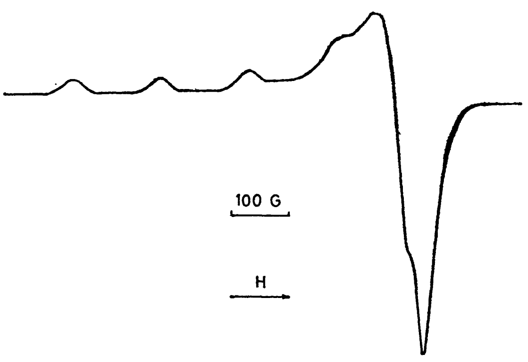
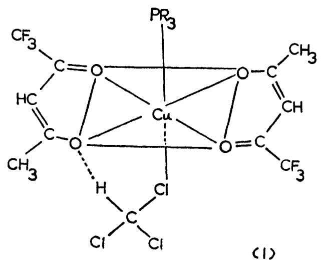
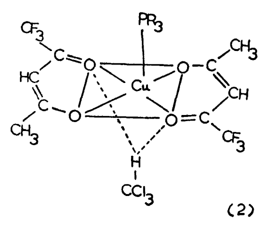


Fig. 2. ESR spectrum of bis(trifluoroacetylacetonato)copper-(II)-dimethylphenylphosphine complex at 77°K in chloroform.

The spectra of bis(trifluoroacetylacetonato)copper-(II)-phosphorus complexes characterise the interaction of the unpaired electron of Cu(II) (nuclear spin $I=3/2$) with one ^{31}P nucleus ($I=1/2$), this interaction being responsible for the doublet splitting of the four copper lines. Due to the overlapping of $+3/2$ and $+1/2$ hyperfine lines of the one with $-3/2$ and $-1/2$



(1)



(2)

TABLE 1. ESR SPECTRA PARAMETERS OF 10^{-3}M SOLUTIONS OF BIS(TRIFLUOROACETYLACETONATO)-COPPER(II) AND BIS(TRIFLUOROACETYLACETONATO)COPPER(II)-PHOSPHORUS COMPLEXES IN CHLOROFORM. HYPERFINE TENSOR COMPONENTS ARE IN UNITS OF 10^{-4}cm^{-1}

Ligand	$<g>$	$<A>$	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$(Cu)	$A_{\perp}$(Cu)	$A_p(^{31}\mathrm{P})$	ΔHNP
$CHCl_3$[a]	2.128	69.9	2.300	2.042	168.2	20.8	—	
Et_3P	2.0901	54.2	2.1978	2.0363	127.8	14.5	119.1	111
(n-Bu)$_3$P	2.1128	54.0	2.1923	2.0231	119.5	19.9	116.9	131
Me_2PPh	2.0864	51.2	2.2113	2.0363	130.4	7.8	110.4	281
$MePPh_2$	2.0929	43.4	2.1985	2.0401	118.4	3.0	82.3	
Ph_3P	2.0942	59.4	2.2031	2.0397	124.4	24.2	—	573
(PhO)$_3$P	2.1067	51.2	2.2207	2.0497	128.1	9.5	—	875

a) from Ref. 13.

lines of the other, a typical six lines spectra are observed. When the phosphine is triphenylphosphine, the ESR spectra of the complexes in chloroform consist mainly of the unresolved four copper lines, but the greater g and smaller A compared with Cu(tfac)$_2$ imply the axial ligation of phosphorus ligand.[12] From the data in Table 1, we suggest the structure of (1) and (2) as in the following diagram, where the chloroform molecule is linked to the metal *via* one of its chlorines[4] or bonded to a pair of the ligand oxygen atoms *via* hydrogen atom.[16] The evidence for the formation of six coordinate bis adducts in bis(trifluoroacetylacetonato)-copper(II) has been found in other case[5] and bis adducts of square planar Ni(II) complexes are common.[14,15] Observations of the X-band spectra of a series of Cu(II) β-diketonates in chloroform-toluene glasses[12] have shown that the exhibition had twice the number of expected lines. This is due to the formation of weak chloroform complexes with some square planar compounds of copper(II).

Our results indicate that phosphines are better ligands towards bis(trifluoroacetylacetonato)copper(II) than the corresponding phosphites. Since phosphite is better π-bonder and poorer σ-donor than phosphine, it follows that the σ-bonding tendency of a ligand is a predominant factor in determining its reactivity. The data in Table 1 also indicate that in phosphine series, the A_P, decreases with increasing basicity of the ligand in the order $Et_3P > (n\text{-}Bu)_3P > Me_2PPh \gg MePPh_2 \gg PPh_3 > P(OPh)_3$. The relative basicities of the phosphines were measured by Streuli,[17] using nitromethane as a solvent and recording the difference in half-neutralization potentials, ΔHNP, with N,N'-diphenylguanidine as a standard. The electron involved in π and σ-bonding between transition metal and phosphine is shifted more toward the phosphorus atom. The highest occupied molecular orbital of the above complexes, which contain an unpaired electron, seems to reflect the general donor-acceptor properties of the ligands.

As predicted from the molecular orbital calculations,[12] the axial ligation results in decreasing separations of ΔE_{xy} and ΔE_{xz}, which yield the differences in the ESR parallel components of the g and hyperfine tensors. The decrease in both $A_{\parallel}$ and $g_{\parallel}$ values from bis(trifluoroacetylacetonato)copper(II) to 1:1 phosphine adduct illustrates the coordination effect. Such phenomena were previously attributed to the solvent effect. Dimerization is also expected to reduce the value of hyperfine tensor in a manner similar to the formation of 1:1 adduct. However, in a dimer, two copper(II) ions ($S=1/2$) are coupled together by a dipolar interaction, a singlet ($S=0$) and triplet ($S=1$) state will be formed and the dipolar interaction will cause a separation of the $M_s=1$ and $M_s=0$ levels in zero magnetic field. ESR transitions are observed within the triplet. These will be in either normal or allowed $\Delta M=1$ type centered about a resonance position H_0, and in addition one may find forbidden or $\Delta M=2$ transition occurring at about $H_0/2$. The absence of low field signal in ESR spectrum of bis(trifluoroacetylacetonato)copper (II)-phosphorus complexes reveals that the changes in ESR parameters can thus be ascribed to differences in the monomer and not to partial dimer.

Attempts to synthesize 1:2 complexes of bis(trifluoroacetylacetonato)copper(II) and phosphine were unsuccessful. The reactions led to the formation of Cu(I) complexes as Cu(tfac)(PR$_3$)$_2$.

The above experimental evidence indicates the formation of 1:1 adduct of bis(trifluoroacetylacetonato)-copper(II) and tertiary phosphines. Further systematic investigations of interaction between β-diketone transition metal complexes and phosphorus ligands are in progress.

Partial financial support by the California State University at Long Beach Foundation is gratefully acknowledged.

---

14) G. N. La Mar, *Inorg. Chim. Acta*, **3**, 183 (1969).

15) R. L. Carlin and A. E. Siegel, *Inorg. Chem.*, **9**, 1587 (1970).

16) E. Sinn, *Inorg. Nucl. Chem. Lett.*, **6**, 811 (1970).

17) C. A. Streuli, *Anal. Chem.*, **32**, 985 (1960).