含硫、磷配位基之單核鈷和混價雙核鈷的製備和反應性探討

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摘要：

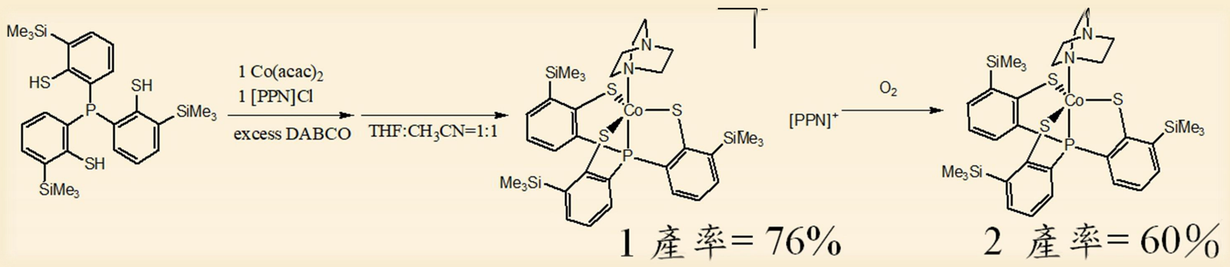
文獻中提到Co^{II}有機會與氧氣反應形成Co^{III}超氧再形成過氧。[1]

本實驗室先前合成[PPN][Mn^{II}($^{TMS}PS_3$)(DABCO)]加入氧氣後可形成[PPN][Mn^{IV}(O_2)($^{TMS}PS_3$)]。[2]

我們嘗試將中心金屬換成Co，合成出Co^{II}–DABCO、Co^{III}–R (R=DABCO、Cl)以及Co^{II}–Co^{III}，其配位環境皆為$^{TMS}PS_3$[3]。

實驗與結果：

合成[PPN][Co^{II}(DABCO)$^{TMS}PS_3$]、Co^{III}(DABCO)$^{TMS}PS_3$



1 產率= 76%　　2 產率= 60%

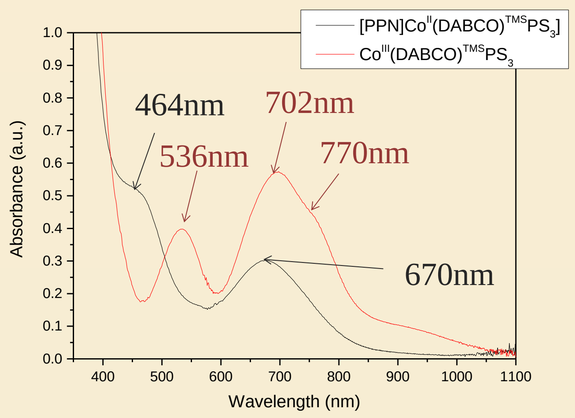


圖1 UV-Vis 光譜圖_1(黑)、2(紅)

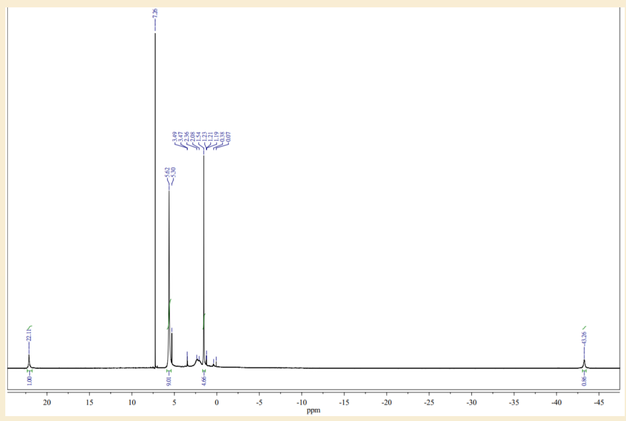
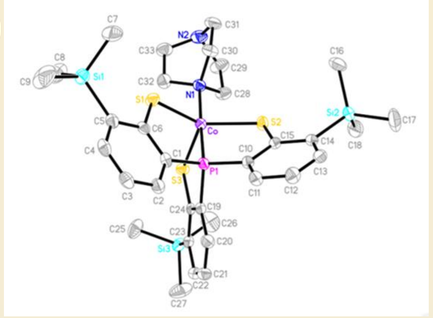
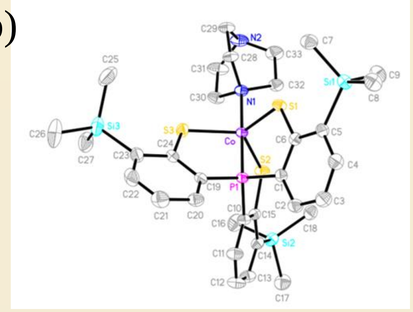


圖2 ^{1}H-NMR 光譜圖_2 in $CDCl_3$



(a)



(b)

圖3 X-ray 晶體結構圖_(a)1 (b)2

Co 和相鄰元素的鍵長[Å]

	1	2
Co–N(1)	2.067(3)	2.068(2)
Co–P(1)	2.0973(9)	2.1395(7)
Co–S(1)	2.2762(9)	2.2331(7)
Co–S(2)	2.2956(9)	2.2371(7)
Co–S(3)	2.3445(8)	2.2421(8)

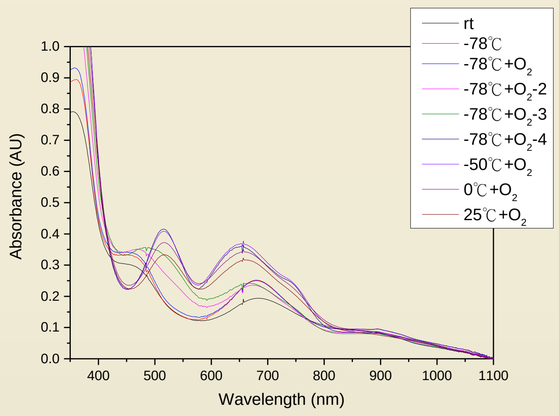


圖4 UV-Vis光譜圖_1於-78℃加O_2

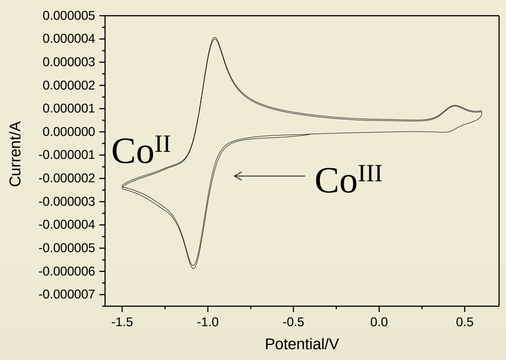
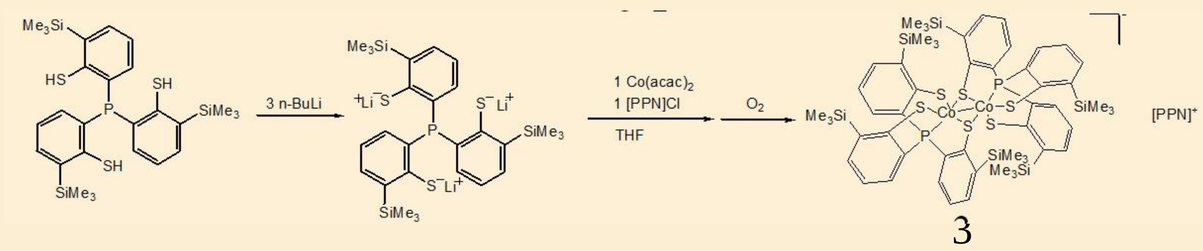


圖5 CV光譜圖_1

合成[PPN][$Co^{II}Co^{III}$($^{TMS}PS_3$)$_2$]



3

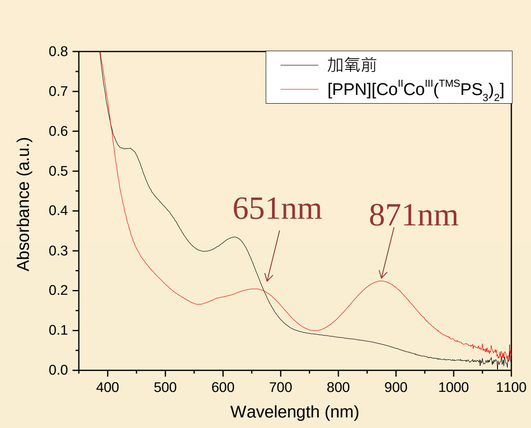


圖6 UV-Vis 光譜圖_3(紅)

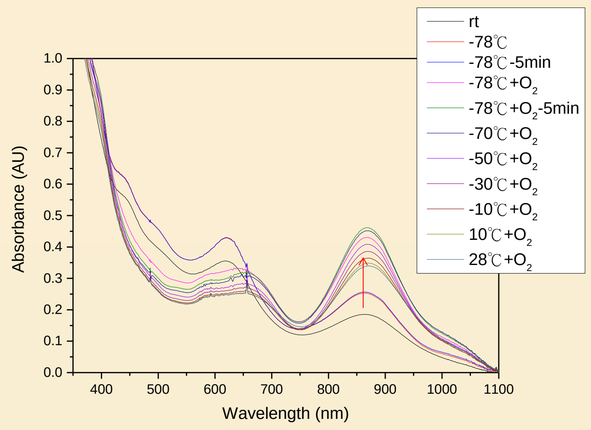
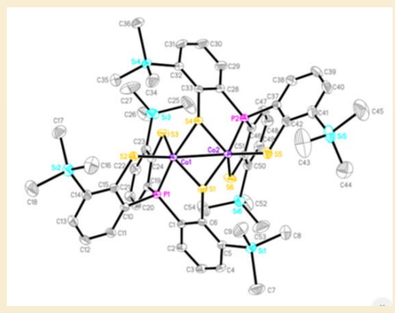


圖7 UV-Vis 光譜圖_3於-78℃加O_2



Co(1)-Co(2) 2.5602(5) Å

圖8 X-ray 晶體結構圖_3

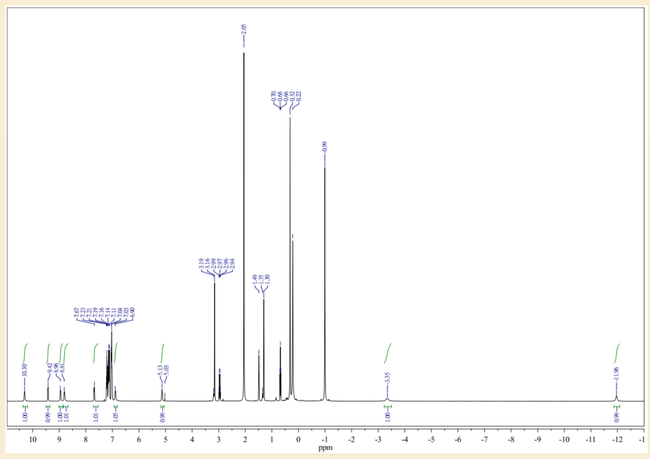
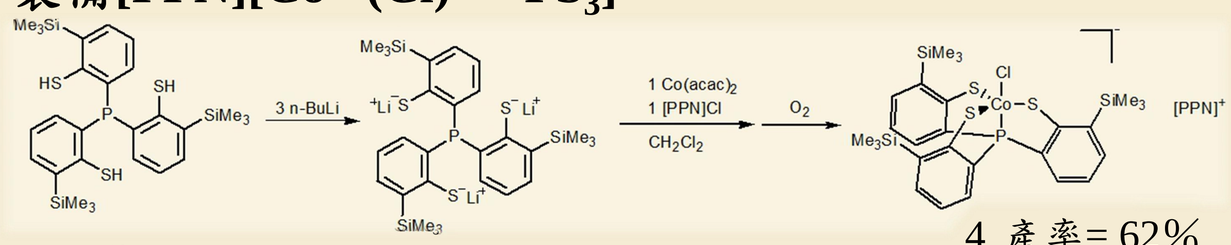


圖9 ^{1}H-NMR 光譜圖_3 in CD_3CN+d_8-THF

製備[PPN][Co^{III}(Cl)$^{TMS}PS_3$]



4 產率= 62%

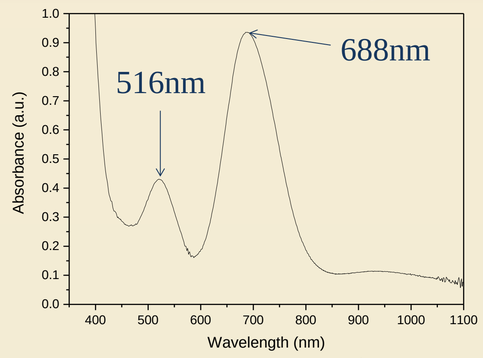


圖10 UV-Vis 光譜圖_4

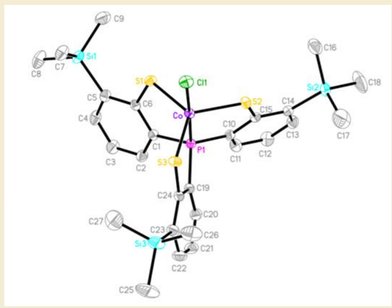


圖12 X-ray 晶體結構圖_4

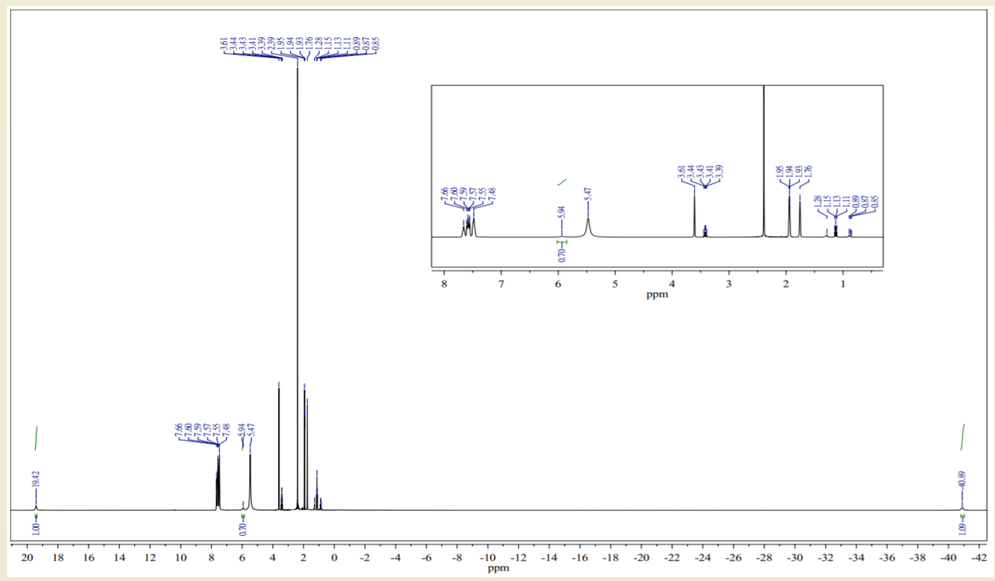


圖13 ^{1}H-NMR 光譜圖_4 in CD_3CN+d_8-THF

結論：

本實驗用$^{TMS}PS_3$為配位基合成出了3種單核鈷錯合物以及1種混價雙核鈷錯合物，都有良好的產率，並藉由光譜來鑑定其性質。

Co^{III}(DABCO)$^{TMS}PS_3$藉由循環伏安法測定，發現Co^{III}可還原為Co^{II}，再由Co^{II}氧化為Co^{III}，形成一個可逆氧化還原。

將[PPN][Co^{II}(DABCO)$^{TMS}PS_3$]與[PPN][$Co^{II}Co^{III}$($^{TMS}PS_3$)$_2$]氧化前化合物於-78℃下加入氧氣，皆沒有發現中間體的存在。

參考文獻：

[1] Lee, C. M.; Wu, W. Y.; Chiang, M. H.; Bohle, D. S.; Lee, G. H. *Inorg. Chem.* **2017**, 56, 10559.

[2] Wang, C. C.; Chang, H. C.; Lai, Y. C.; Fang, H.; Li, C. C.; Hsu, H. K.; Li, Z. Y.; Lin, T. S.; Kuo, T. S.; Neese, F.; Ye, S.; Chiang, Y. W.; Tsai, M. L.; Liaw, W. F.; Lee, W. Z. *J. Am. Chem. Soc.* 2016, 138, 1418.

[3] Block, E.; Ofori-Okai, G.; Zubieta, J. *J. Am. Chem. Soc.* **1989**, 111, 2327