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Cyclopentadienyl Vanadium Complexes: Di-μ-methylsulfide-bis(dicarbonylcyclopentadienylvanadium)

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The widespread interest in polymetallic carbonyl complexes [1–3], and the few results in the vanadium chemistry prompt us to report the preparation of a new dinuclear vanadium complex $[V_2(\eta^5\text{-}C_5H_5)_2(SMe)_2(CO)_4]$ (I). Most of the bimetallic compounds have two active sites and are generally very reactive [1]. The thio-bridged molybdenum or tungsten $[M_2(\eta^5\text{-}C_5H_5)_2(SR)_2(CO)_4]$ (M = Mo or W; R = Me or CF_3) [4] and iron $[Fe_2(\eta^5\text{-}C_5H_5)_2(SR)_2(CO)_2]$ (R = Me or CF_3) [5] without metal–metal bond complexes have already been obtained. Several monomeric thio-vanadium species $[V(\eta^5\text{-}C_5H_5)_2(SR)]$ (R = Me, Et, Ph or $PhCH_2$), $[V(\eta^5\text{-}C_5H_5)_2(SR)_2]$ (R = Ph) and $[V(\eta^5\text{-}C_5H_5)_2(SR)(CO)]$ (R = Me or Ph) are known [6]. The first dimeric thio-bridged vanadium compounds described are $[V_2(\eta^5\text{-}C_5H_5)_2(SR)_4]$ (R = Me [7] (II) or Ph [8]), but there has so far been no report of a dimeric carbonyl thio-bridged vanadium complex with metal–metal bond.

On photolysis in tetrahydrofuran at room temperature for about four days in Pyrex apparatus bis(methyl)disulphide gives complexes (I) and (II) with $[V(\eta^5\text{-}C_5H_5)(CO)_4]$. (I) and (II) are separated by chromatography on a florisil column and are obtained in the respective yields 21–68% and 8–59% according to time irradiation; (II) is the main product when the time reaction is less than three days.

Recrystallization of the complex (I) from dichloromethane–n-hexane gives orange-brown crystals whose elemental analysis indicates a cyclopentadienyl/carbonyl/methylsulfide/vanadium ratio of 1:2:1:1. *Anal.* Found: C, 42.9; H, 3.93; S, 14.5; V, 22.8. Calcd. for $C_{16}H_{16}O_4S_2V_2$: C, 43.8; H, 3.67; S, 14.6; V, 23.2. The compound is formulated as a dinuclear complex on the basis of its molecular weight (393; osmometric in $CHCl_3$) and its mass spectrum (m/e: 438 $[V_2(\eta^5\text{-}C_5H_5)_2(SMe)_2(CO)_4]^+$, 382 $[V_2(\eta^5\text{-}C_5H_5)_2(SMe)_2(CO)_2]^+$, 354 $[V_2(\eta^5\text{-}C_5H_5)(SMe)_2(CO)]^+$, 344 $[V_2(\eta^5\text{-}C_5H_5)_2(CO)_4]^+$, 219 $[V(\eta^5\text{-}C_5H_5)(SMe)(CO)_2]^+$. The infrared spectrum (in CCl_4) shows two strong $\nu C{\equiv}O$ bands at 1937 and 1995 cm^{-1} consistent with the structure depicted in Fig. 1.

NMR spectroscopy is also helpful in assigning the structure of the derivative (I). The presence of two cyclopentadienyl resonances {^1H NMR $[(CD_3)_2CO]$, δ at 2.26 (s, CH_3) and 5.20 (s), 5.23 (s) ppm/TMS $(\eta^5\text{-}C_5H_5)$; ^{13}C NMR $[(CD_3)_2CO]$, δ at 23.71 (CH_3) and 94.79, 94.53 ppm/TMS $(\eta^5\text{-}C_5H_5)$, the relaxation time of the vanadium does not permit to observe the carbonyl peak even at low temperature} suggests either an asymmetrical structure or more likely a mixture of isomers. These hypothetical isomers do not interconvert between 181 and 327 K.

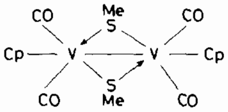

Fig. 1. Suggested structure for (I).

Complex (I) is stable to air in the solid only for a few minutes and decomposes quickly in solution on exposure to air giving a not well defined black compound whose infrared spectrum contains no $\nu C{\equiv}O$ band but a strong peak at 960 cm^{-1} compatible with a $\nu V{=}O$.

When (I) is treated with CS_2 (2 h at 25 °C) in toluene the solution turns from orange to brown. Evaporation of the solvent leaves a dark-brown solid, the infrared spectrum of which shows the presence of a large νCS band at 1100 cm^{-1} and of no $\nu C{\equiv}O$ peak. (I) reacts also with iodine.

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References

1 R. Poilblanc, *Nouv. J. Chim.,2,* 145 (1978) (and references therein).
2 N. E. Schore, C. S. Iienda and R. G. Bergman, *J. Am. Chem. Soc., 99,* 1781 (1977).
3 R. J. Lawson and J. R. Shapley, *J. Am. Chem. Soc., 98,* 7433 (1976).
4 P. M. Treichel, J. H. Morris and F. G. A. Stone, *J. Chem. Soc.,* 720 (1963); R. Havlin, G. R. Knox, *Z. Naturforsch., 21b,* 1108 (1966); D. D. Watkins, Jr., and T. A. George, *J. Organometal. Chem., 102,* 71 (1975); J. L. Davidson and D. W. A. Sharp, *J. Chem. Soc. Dalton,* 107 (1972).
5 R. B. King, P. M. Treichel and F. G. A. Stone, *J. Am. Chem. Soc., 83,* 3600 (1961); J. L. Davidson and D. W. A. Sharp, *J. Chem. Soc. Dalton,* 1957 (1973).
6 G. Fachinetti and C. Floriani, *J. Chem. Soc. Dalton,* 2433 (1974).
7 R. H. Holm, R. B. King and F. G. A. Stone, *Inorg. Chem., 2,* 219 (1963).
8 A. A. Pasynskii, I. L. Eremenko, V. M. Novotortsev, Y. V. Rakimen, O. G. Ellert and V. T. Kalinnikov, *Izv. Akad. Nauk. SSSR, Ser. Khim.,* 1900 (1976).