TABLE III

^{27}Al CHEMICAL SHIFTS AND LINE WIDTHS FOR SOLUTIONS OF ALUMINUM COMPOUNDS AT 12.0 Mc

Compound	Solvent	Chemical shift ± 5 cps	Line width, cps
$Al(ClO_4)_3$ (0.20 m)	DMF	+990	39 ± 2
$Al(ClO_4)_3$ (satd)	H_2O	+970	55 ± 2
$Al(acac)_3$ (1.0 m)	Benzene	+940	120 ± 2
$KAl(OH)_4$ (0.20 m)	Aqueous KOH	...	200 ± 5

tions of $Al(acac)_3$, which has a D_3 perturbation upon its grossly octahedral geometry, and $Al(OH)_4^-$, which is tetrahedral, demonstrate how marked the broadening is with the lowering of symmetry.

These studies are now being extended to mixed complexes of the type $Al(DMF)_{6-n}X_n^{3-n}$, utilizing both the proton and ^{27}Al resonances.

Experimental Section

Acetylacetone (2,4-pentanedione) was obtained from Matheson Coleman and Bell and distilled before use. Eastman White Label N,N-dimethylformamide (DMF) was purified in the manner previously described.[1] Aluminum trisacetylacetonate was prepared by dissolving stoichiometric amounts of $Al(ClO_4)_3$ and acetylacetone in water and neutralizing the resulting solution with aqueous ammonia. The precipitate which formed was separated by filtration and recrystallized from a benzene-petroleum ether (bp 67–92°) solution. The complex $Al(DMF)_6(ClO_4)_3$ was prepared from $Al(ClO_4)_3 \cdot 9H_2O$ (G. F. Smith Chemical Co.) using the method of Drago, *et al.*[17] *Anal.* Calcd for $Al(DMF)_6(ClO_4)_3$: Al, 3.52; ClO_4, 39.1. Found: Al, 3.4; ClO_4, 39.2.

The proton nmr spectra were obtained at 100 Mc using a Varian HA-100 spectrometer operated in the HR mode. The spectrometer was equipped with a variable-temperature probe and the Varian variable-temperature control system, V-6057. The system was calibrated and the measurements were obtained in the manner described previously.[1] The line widths were reproducible to within ±0.2 cps.

The ^{27}Al nmr spectra were obtained at 12 Mc using a Varian HR-40 spectrometer equipped with a 12-Mc probe and radiofrequency unit. The magnetic field was calibrated with an audio oscillator monitored by a frequency counter. Each of the line widths and chemical shifts reported is the average obtained from four spectra. The chemical shifts were obtained using an aqueous solution of potassium tetrahydroxoaluminate(III) as the external standard.

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(17) R. S. Drago, M. D. Joesten, and L. LaRoche, *Inorg. Chem.*, **2**, 124 (1963).

CONTRIBUTION FROM THE CENTRAL RESEARCH DIVISION, AMERICAN CYANAMID COMPANY, STAMFORD, CONNECTICUT

Bis(cyclopentadienyl)titanium(IV) Compounds with Sulfur-Containing Groups[1]

BY S. A. GIDDINGS

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Transition metals to the left of the periodic table are considered to be type A using the Chatt[2] designation or to be "hard" acids in the Pearson[3] designation. Titanium(IV) would have to be considered typical of the above as it has no d electrons and thus should not be able to enter into $d\pi$–$d\pi$ back bonding with donors such as sulfur- and phosphorus-containing ligands which have empty d orbitals. It would be expected to form compounds more readily with oxygen and nitrogen donors (hard bases). Obvious attempts to form bis(cyclopentadienyl)titanium diethoxide were unsuccessful[4,5] using a variety of approaches. Efforts to prepare the diphenoxide by the author also proved unsuccessful and will be reported elsewhere. This paper reports the synthesis of the dimercaptide derivatives of bis(cyclopentadienyl)titanium and an investigation of the dithiocyanate derivative.

Experimental Section

All glass apparatus was thoroughly dried and rections were carried out under dry argon unless noted. Solvents were dried by standard procedures.

a. **Preparation of Bis(cyclopentadienyl)titanium Dimethylmercaptide.**—A 2-ml amount (excess) of methanethiol (Eastman) was added to 0.3 g of sodium (0.013 g-atom) in 50 ml of dry ether. A Dry Ice condenser was used along with a trap containing pellets of KOH to prevent escape of traces of the malodorous thiol. The mixture was stirred at room temperature for 3 days and then 50 ml of toluene was added, followed by bis(cyclopentadienyl)titanium dichloride (1.25 g, 0.005 mole). Stirring was continued for 3 hr and the red solution turned burgundy in color. The mixture was heated to the reflux temperature of toluene and was then filtered while still hot. On cooling overnight, at 0° deep burgundy crystals (0.82 g, yield 60%) were obtained, mp 193–197°. *Anal.* Calcd for $C_{12}H_{16}S_2Ti$: C, 52.76; H, 5.91; S, 23.55. Found: C, 53.43; H, 5.54; S, 23.20.

b. **Preparation of Bis(cyclopentadienyl)titanium Didodecylmercaptide.**—Dodecanethiol (Eastman 3.03 g, 0.015 mole) was mixed with 25 ml of dry benzene and 5 ml triethylamine. Bis(cyclopentadienyl)titanium dichloride (1.87 g, 0.0075 mole) was added to the above mixture which was then brought to reflux and maintained for 1 hr. The reaction mixture was filtered while hot and the filtrate was evaporated to dryness. The solid obtained was treated with hot hexane and filtered, and the filtrate was reduced in volume. A solid product appeared when the solution was cooled to 0°; it could not be filtered at room temperature as it tended to melt. Filtration at 0° gave 4.50 g of a deep burgundy material which melted on warming to room temperature. Purification of this material was not possible but infrared spectra showed no unusual bands.

c. **Preparation of Bis(cyclopentadienyl)titanium Diphenylmercaptide.**—Bis(cyclopentadienyl)titanium dichloride (2.49 g, 0.01 mole) was dissolved in a solution of 90 ml of toluene and 10 ml of triethylamine. Thiophenol (2.204 g, 0.02 mole) was added; the mixture was stirred for 2 hr at room temperature and then heated at reflux temperature for 30 min. The reaction mixture was filtered while still hot and the solvent was then stripped from the filtrate. The solid obtained was then recrystallized from toluene; yield, 3.40 g (86%) of very deep burgundy crystals, mp 199–201°. *Anal.* Calcd for $C_{22}H_{20}TiS_2$: C, 66.57; H, 5.10; S, 16.17; mol wt, 396.4. Found: C, 66.52; H, 5.25; S, 16.26; mol wt, 395 (in benzene).

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(1) Presented in part at the 2nd International Conference on Organometallic Chemistry, Madison, Wis., Aug 29–Sept 3, 1965.

(2) S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.* (London), **12**, 265 (1958).

(3) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).

(4) A. N. Nesmeyanov, O. V. Nogina, and A. M. Berlin, *Dokl. Akad. Nauk SSSR*, **134**, 607 (1960).

(5) A. N. Nesmeyanov, O. V. Nogina, A. M. Berlin, A. S. Girshovich, and G. V. Shatalov, *Izv. Akad. Nauk SSSR*, 2146 (1961).

The magnetic susceptibility was found to be -85.7×10^{-9} cgs unit at 27.0°, typical for a titanium(IV) d^0 species.

d. **Preparation of Bis(cyclopentadienyl)titanium Dithiocyanate.**—Potassium thiocyanate (2.13 g, 0.022 mole) and bis(cyclopentadienyl)titanium dichloride (2.49 g, 0.01 mole) were added to 50 ml of acetone and the mixture was heated at reflux temperature for 2 hr. Excess thiocyanate and potassium chloride were filtered from the hot solution and, on cooling, brick red crystals (2.32 g, 79% yield) formed, which were recovered by filtration, mp 303–307° with decomposition. *Anal.* Calcd for $C_{12}H_{10}N_2S_2Ti$: C, 49.0; H, 3.43; N, 9.52; S, 21.8. Found: C, 49.3; H, 3.56; N, 9.65; S, 21.5.

e. **Reaction of Bis(cyclopentadienyl)titanium Dithiocyanate with *n*-Butylamine.**—*n*-Butylamine (0.292 g, 0.004 mole) was added slowly to a stirred solution of the dithiocyanate (0.588 g, 0.002 mole) in 20 ml of acetone in an open beaker. The solution turned to orange from the original magenta color. The reaction was stirred at room temperature for 2 hr. After reducing the solution volume to 7 ml, 0.25 g (60%) of orange crystals deposited and was collected by filtration. The orange crystals melted at 235–238° with decomposition and had an infrared spectrum similar to the dithiocyanate (II) but with the addition of a strong band at 730 cm^{-1} assigned to a Ti–O–Ti stretch. The analysis confirmed the formation of the oxydimer $(TiCp_2CNS)_2O$. *Anal.* Calcd for $C_{22}H_{20}N_2S_2Ti_2O$: C, 54.10; H, 4.12; N, 5.73; S, 13.13. Found: C, 53.77; H, 3.99; N, 5.57; S, 13.06.

When the same quantities of II and butylamine were refluxed in dry toluene for 3 hr under an argon atmosphere, 0.51 g of II was recovered and only minute quantities of the oxydimer could be detected.

f. **Hydrolysis of Bis(cyclopentadienyl)titanium Dimercaptides.**—Mercaptide derivatives (0.1 g) were dissolved in 25 ml of acetone containing 1 ml of water at room temperature. The dodecyl compound was hydrolyzed to a yellow precipitate in 2 hr, the methyl was hydrolyzed in 30 hr, and no change was observed with the phenyl derivative in 3 days.

The yellow precipitates were examined by infrared spectrophotometry and were similar to those obtained in earlier attempts to prepare the titanoxane polymer $[TiCp_2O]_n$.[6] The analysis (C, 30.11, 23.89; H, 3.76, 3.56) for the products obtained from the dodecyl and methyl mercaptides also showed the loss of cyclopentadienyl groups.

Discussion

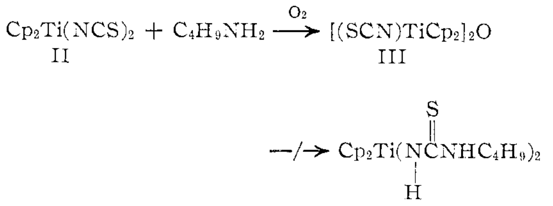
Bis(cyclopentadienyl)titanium mercaptides (I) were formed *via* the reaction

$$Cp_2TiCl_2(I) + RSH + \text{base} \longrightarrow Cp_2Ti(SR)_2 + HCl\cdot\text{base}$$

where R = methyl, *n*-dodecyl, or phenyl. The reaction proved to be successful with metallic sodium or triethylamine as base. This was unexpected[7] in view of the problem associated with the isolation of dialkoxide.[4,5] More recently[8] their ready formation and stability have been observed independently.

This is all the more remarkable when it is considered that elements to the left of the periodic table in the transition series (titanium is extreme left) normally tend to form more stable compounds with oxygen- rather than sulfur-containing liquids. Stronger bonds with the sulfur compounds are considered to form when the metal has an excess of electrons which can be donated into the empty d orbitals of sulfur (back bonding). Thus in this case we can only assume that the back bonding is possible because of the overlap of the π orbitals of the cyclopentadienyl ion with the preferred titanium d orbitals; the electrons are then delocalized through the remaining d orbitals of titanium, followed by donation into the empty d orbitals of sulfur.

As a consequence of the stability of the mercaptides it was of interest to know whether the dithiocyanate (II) was bonded through the S atom. Also, if II were to have the iso structure it would be of interest as a potential monomer for the preparation of polythioureas or thiocarbamates containing bis(cyclopentadienyl)titanium groups in the backbone. In a diagnostic model reaction with butylamine, none of the thiourea was formed. The only product was the oxydimer III (60%) when the reaction was run in an open vessel; reaction in an inert atmosphere followed by workup in air gave a lower yield of III along with 80% of recovered II.



$$\underset{\text{II}}{Cp_2Ti(NCS)_2} + C_4H_9NH_2 \xrightarrow{O_2} \underset{\text{III}}{[(SCN)TiCp_2]_2O}$$

$$\not\longrightarrow Cp_2Ti(\underset{\displaystyle H}{\underset{|}{N}}\overset{\displaystyle S}{\overset{\|}{C}}NHC_4H_9)_2$$

Compound III was apparently formed by reduction of II by the amine followed by air oxidation or by hydrolysis and condensation.

Whether the thiocyanate derivative of bis(cyclopentadienyl)titanium had the iso or normal thiocyanate structure could not be determined unequivocally by infrared spectroscopy. The C–N stretching frequency is relatively insensitive to the structural isomerism and hence would not be useful. Carbon–sulfur stretching frequencies for M–SCN have been shown[9] to lie within the region 690–720 cm^{-1}, as compared to 780–860 cm^{-1} for M–NCS. However, these bands are normally weak, and the sharp band due to the cyclopentadienyl group at 830 cm^{-1} reduces the chance of observing the M–NCS region. A very weak, broad band at 720 cm^{-1} may indicate M–SCN bonding but again could hardly be used as proof of structure and could possibly be due to traces of the impurity $[TiCp_2CNS]_2O$ which has a strong band at 730 cm^{-1}. Raman spectroscopy, which would differentiate the structures, could not be applied owing to the intense color of the solution. The question of structure was thus not settled but color, lack of reaction with butylamine, and to a lesser extent infrared spectra indicate bonding through the S atom.

Attempts to form the thiobenzoate derivative using toluene as solvent and sodium thiobenzoate in air produced $C_6H_5C(O)–S–S–C(O)–C_6H_5$ and some yellow precipitate identified as the partial decomposition product of $[TiCp_2O]_n$.[6]

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[6] S. A. Giddings, *Inorg. Chem.*, **3**, 684 (1964).

[7] S. A. Giddings, U. S. Patent 3,030,395 (1962).

[8] F. G. A. Stone, private communication.

[9] F. Basolo, J. L. Burmeister, and A. J. Poe, *J. Am. Chem. Soc.*, **85**, 1708 (1963).