indium is pentacoordinate, with three short In–C bonds and two larger intermolecular contacts. In $In(Ph)_3$, bonds from the metal to the α carbon of phenyl groups on two neighboring molecules together with three planar In–C bonds again result in a coordination number of five.[5] These conclusions, and the present structure, are in agreement with results for InX_3 (X = halide or pseudohalide) species, where the three-coordinate monomer readily undergoes dimerization or adduct formation to give coordination numbers of four, five, or six.[4] The electron deficiency is however apparently unique to the three organoindium compounds in this context. It may be that this can be regarded as a type of electron donation in which the donor is not in its ground state, as is usually assumed for (say) a pyridine adduct, but in some electronically excited state. Thus in $In(cp)_3$, the diene structure (rings B and C) represents the first excited state of the cyclopentadienyl group, while the structure of ring A corresponds to the second excited level. Indium(I) cyclopentadienyl, in contrast apparently involves the ground-state (symmetrical) structure of the ligand. Further work on this problem is planned.

Acknowledgments.—The authors wish to thank Dr. P. G. Lenhert for making available his diffractometer control programs, and the National Research Council of Canada for support in the form of Operating Grants.

Notes

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MCMASTER UNIVERSITY, HAMILTON, ONTARIO, CANADA

Adducts between Tetrasulfur Tetranitride and Aluminum Halides

BY C. H. CHAN AND F. P. OLSEN*

Received February 25, 1972

Molecular 1:1 adducts are formed between tetrasulfur tetranitride and a variety of Lewis acids.[1] Crystallographic data on two of these, $S_4N_4 \cdot SbCl_5$[2] and $S_4N_4 \cdot BF_3$,[3] have shown them to retain the eight-membered S_4N_4 ring, but with a conformation in which the sulfur and nitrogen positions are approximately interchanged. The four sulfur atoms lie in the plane and the four nitrogen atoms form the bisphenoid with the Lewis acid bonded to nitrogen. Aluminum chloride, on the other hand, reacts[4] with tetrasulfur tetranitride in thionyl chloride to give a salt, $S_5N_5{}^+AlCl_4{}^-$, rather than a molecular adduct. We describe here the preparation of simple 1:1 adducts between tetrasulfur tetranitride and aluminum halides.

Results and Discussion

Tetrasulfur tetranitride and aluminum chloride reacted slowly at room temperature in 1,2-dichloroethane to give a deep red crystalline product whose elemental analysis corresponded to that of a 1:1 adduct. This material was very sensitive to moisture and underwent hydrolysis in air to give tetrasulfur tetranitride which could be recovered in 95% yield from the adduct. The material decomposed on attempted vacuum sublimation to give a gummy intractable product. The infrared spectrum showed strong absorption at 1045, 960, and 860 cm^{-1} assignable[5,6] to sulfur–nitrogen absorption, as well as a strong band at 500 cm^{-1} assignable[7] to an aluminum–nitrogen stretch. The similarity between the ir spectrum of $S_4N_4 \cdot AlCl_3$ and those[1] of $S_4N_4 \cdot SbCl_5$ and $S_4N_4 \cdot BF_3$ strongly suggests an analogous structure for the three compounds. The aluminum chloride adduct also resembles $S_4N_4 \cdot BCl_3$ in adding a further mole of antimony pentachloride.[1,8] This material of composition $S_4N_4 \cdot AlCl_3 \cdot SbCl_5$ could be prepared from either antimony pentachloride and $S_4N_4 \cdot AlCl_3$ or aluminum chloride and $S_4N_4 \cdot SbCl_5$. An attempt to displace aluminum chloride from the mixed diadduct by vacuum sublimation led mainly to decomposition. Only very small traces of $S_4N_4 \cdot SbCl_5$ could be recovered in this manner. This is in contrast to $S_4N_4 \cdot BCl_3 \cdot SbCl_5$ where[1] boron trichloride is lost on heating to 85–90° under vacuum.

A similar 1:1 adduct between aluminum bromide and tetrasulfur tetranitride was observed to form upon mixing the two materials in 1,2-di*bromo*ethane. In 1,2-di*chloro*ethane, however, aluminum bromide and tetrasulfur tetranitride gave only $S_4N_4 \cdot AlCl_3$. Since a sample of $S_4N_4 \cdot AlBr_3$ was recovered unchanged after refluxing for 36 hr in 1,2-dichloroethane, exchange of halide with solvent must have occurred in the free aluminum bromide prior to complex formation. The exchange of halide between aluminum bromide and chloroalkanes is expected[9] to occur in the absence of S_4N_4. There can be no significant amount of reversible dissociation of the adduct once it is formed. This result is consistent with the failure to recover either starting materials or the adduct on attempted sublimation. It is in contrast to the behavior of $S_4N_4 \cdot BF_3$ where[1] boron trifluoride and tetrasulfur tetranitride can be recovered on thermal decomposition *in vacuo* (although the S_4N_4 ring does not survive when the adduct is heated in a sealed tube). $S_4N_4 \cdot BCl_3$, on the other hand, undergoes sublimation at 115°.

The minimal success in displacing aluminum chloride from $S_4N_4 \cdot AlCl_3 \cdot SbCl_5$, the failure of bromide to ex-

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change with the solvent in $S_4N_4 \cdot AlBr_3$ and the inability to recover aluminum chloride from attempted sublimation all suggest less ready dissociation in the aluminum halide–tetrasulfur tetranitride adducts than has been observed in the analogous boron trichloride adduct (*i.e.*, a higher formation constant most probably arising from a smaller rate of dissociation).

Experimental Section

General.—Tetrasulfur tetranitride was prepared as previously described[10] and recrystallized from benzene to give material of mp 178°. Aluminum halides were sublimed *in vacuo* immediately prior to use. All solvents were reagent grade, were refluxed over phosphorus pentoxide for 6 hr prior to distillation and were subsequently stored in the drybox. All reactions and work-up procedures were carried out in a Vacuum Atmosphere Corp. Dry Lab, equipped with Dry Train Model HE-93-B. Analyses for carbon, hydrogen, nitrogen, and halogen were performed by commercial laboratories. Sulfur was analyzed in triplicate by conversion to barium sulfate.[11] Aluminum was determined by neutron activation analysis of ^{28}Al.

$S_4N_4 \cdot AlCl_3$.—Aluminum chloride (0.88 g, 6.8 mmol) was added to 50 ml of dry 1,2-dichloroethane, followed by 1.21 g (6.6 mmol) of tetrasulfur tetranitride. The reaction mixture turned dark red immediately. After 5 hr of stirring, no undissolved tetrasulfur tetranitride remained. The deep red solution was filtered and reduced in volume (*in vacuo*) until precipitation began. The solution was then heated to redissolve the product and cooled overnight whereupon dark red crystals were obtained. These were collected by filtration and dried *in vacuo* to give a crystalline product which decomposed at 100° in a sealed tube. The infrared spectra (Nujol mull) showed absorption at 1045 (s), 990 (m), 960 (s), 925 (m), 860 (s), 750 (m), 720 (w), 700 (m), 675 (w), 620 (m), 570 (w, sh), 540 (w, sh), 500 (s), 470 (s, sh), 400 (s), 360 (w), 340 (w), 320 (w) cm^{-1}. *Anal.* Calcd for $S_4N_4AlCl_3$: S, 40.4; N, 17.6; Al, 8.5; Cl, 33.6. Found: S, 40.5; N, 16.0; Al, 8.5; Cl, 34.2.

On exposure of 0.6075 g (1.94 mmol) of the adduct to air, it turned yellow and became sticky. After several days, extraction of this material with benzene gave 0.3372 g (1.83 mmol) of tetrasulfur tetranitride. On contact with water, the adduct underwent rapid decomposition to a dark green intractable slime.

$S_4N_4 \cdot AlCl_3 \cdot SbCl_5$.—Antimony pentachloride (0.90 g, 3.0 mmol) was added to 0.858 g (2.65 mmol) of $S_4N_4 \cdot AlCl_3$ in 20 ml of dry carbon tetrachloride and stirred at room temperature for 5 hr. Filtration gave a light brown powder which was washed repeatedly with dry carbon tetrachloride and dried *in vacuo*. *Anal.* Calcd for $S_4N_4 \cdot AlCl_3 \cdot SbCl_5$: S, 20.8. Found: S, 21.1.

The ir spectra showed bands at 1080 (s), 1010 (w), 995 (m), 825 (m), 800 (m), 740 (w), 720 (w, sh), 530 (s), 360 (s, multiple absorption) cm^{-1}. The powder was placed in a sublimation apparatus and heated to 120° whereupon traces of $S_4N_4 \cdot SbCl_5$ (identified by ir spectra) collected on the cold finger. No $S_4N_4 \cdot AlCl_3$ was observed and the residue consisted mainly of an intractable polymer.

When $S_4N_4 \cdot SbCl_5$ (1.50 g, 3.17 mmol) was stirred with 0.50 g (3.17 mmol) of $AlCl_3$ in 20 ml of dry carbon tetrachloride a similar brown powder resulted whose ir spectrum was superimposable upon that of the previous mixed adduct.

$S_4N_4 \cdot AlBr_3$.—Freshly sublimed aluminum bromide (6.49 g, 24.7 mmol) was reacted with 4.53 g (24.6 mmol) of tetrasulfur tetranitride in 50 ml of dry 1,2-dibromoethane. The reaction mixture slowly turned dark red and, after work-up as described for the chloride, gave orange crystals which decomposed at 122°. The infrared spectra (Nujol mull) showed adsorption at 1035 (s), 950 (s), 850 (s), 830 (s), 770 (m), 715 (w), 515 (s), 480 (s), 440 (w), 380 (s), 350 (w) cm^{-1}. *Anal.* Calcd for $S_4N_4 \cdot AlBr_3$: S, 28.3; N, 12.4; Al, 6.0; Br, 53.3. Found: S, 28.4; N, 12.0; Al, 5.6; Br, 53.4.

A sample (0.1724 g, 0.386 mmol) on exposure to air for several days gave 0.0646 g (0.351 mmol) of tetrasulfur tetranitride on extraction with benzene.

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CONTRIBUTION FROM THE RADIATION CENTER OF
OSAKA PREFECTURE, SHINKE-CHO, SAKAI, OSAKA, 593 JAPAN,
AND THE GOVERNMENT INDUSTRIAL RESEARCH INSTITUTE,
NAGOYA, HIRATE-MACHI, KITA-KU, NAGOYA, 462 JAPAN

Complexes Formed by the Reactions of Tetraoxobis(pyridine)ruthenium(VIII) with 2,2′-Bipyridine and 1,10-Phenanthroline in Methanol

BY TOSHIO ISHIYAMA* AND YOSHIO KODA

Received February 25, 1972

No hydroxoruthenium(II) complexes with pyridine, 2,2′-bipyridine, or 1,10-phenanthroline have previously been reported. Dwyer, *et al.*,[1-3] reported that tetrakis(pyridine)(2,2′-bipyridine)ruthenium(II) perchlorate, $[Ru(py)_4bipy](ClO_4)_2$, was isolated by the addition of pyridine to a hot concentrated solution of acid, $H[RuCl_4bipy]$, and reported that two pyridine molecules in $[Ru(py)_4bipy]^{2+}$ were readily replaced by a variety of other ligands although it was difficult to replace more than two. They also reported that *cis*-bis(pyridine)bis(1,10-phenanthroline)ruthenium(II) perchlorate, *cis*-$[Ru(py)_2phen_2](ClO_4)_2$, was formed by the reaction of $[RuCl_2phen_2]$ with pyridine. In previous papers[4-7] it was reported that $[RuO_4(py)_2]$, $[RuO_4bipy]$, and $[RuO_3phen]_2O$ were obtained by the reactions of ruthenium tetraoxide with pyridine, 2,2′-bipyridine and 1,10-phenanthroline in carbon tetrachloride, respectively, and it was also reported that $[RuO_2(bipy)_2]$, $[RuO_2bipy \cdot phen]$, and $[RuO_2(phen)_2]$ were obtained by the reduction and substitution reactions of $[RuO_4bipy]$ and $[RuO_3phen]_2O$ with 2,2′-bipyridine and 1,10-phenanthroline in methanol, respectively. In the present paper two new complexes, $[Ru(OH)_2(py)_2bipy] \cdot 3H_2O$ and $[Ru(OH)_2(py)_2phen] \cdot 1.5H_2O$, are reported, together with the infrared and electronic spectra and magnetic properties of the starting complex, $[RuO_4(py)_2]$, reported previously.[4]

Experimental Section

Materials.—Ruthenium(III) chloride monohydrate (extra pure grade) supplied by Mitsuwa Chemicals was used as received. Pyridine was treated with potassium permanganate, distilled, treated with potassium hydroxide, and redistilled. Both 2,2′-bipyridine and 1,10-phenanthroline were supplied by Wako Pure Chemical Industries Ltd. The former was purified by recrystallization from distilled water, and the latter from ethanol after it had been dried by heating at 110° for 3 hr. Commercial methanol was dried by treatment with magnesium ribbon and iodine and distilled. Lithium perchlorate (extra pure grade) supplied by Mitsuwa Chemicals was purified by recrystallization from methanol after heating at 110° for 3 hr.

Syntheses. (1) **Tetraoxobis(pyridine)ruthenium(VIII), $[RuO_4(py)_2]$.**—This compound was synthesized according to the method reported previously.[4]

(2) **Dihydroxobis(pyridine)(2,2′-bipyridine)ruthenium(II),**

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* Address correspondence to this author at the Radiation Center of Osaka Prefecture.

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