spectrum exhibited the parent with 1% relative intensity. The peak with the highest intensity was detected at *m/e* 195 with a composition of $C_7H_5OP_2N_2$. An isomeric structure where the oxygen atom migrates into the P–P bond can be excluded because the spin–spin coupling of $^2J_{POP}$ should be 10 times smaller.

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Registry No. **1**, 80049-55-4; **2**, 2303-76-6; **3**, 80049-56-5.

Contribution from the Department of Chemistry,
Indian Institute of Technology, Kanpur 208016, India

First Example of Coordination of the Thionitro Group in a Cobalt Complex. Synthesis and Characterization of $Co(NSO)Cl_2[P(OPh)_3]_2$

R. D. Tiwari, K. K. Pandey, and U. C. Agarwala*

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Although the conversion of a coordinated nitrosyl ligand to a nitro species by molecular oxygen in cobalt nitrosyl complexes is well-known,[1-4] no complex having a coordinated thionitro group (as an N donor) has yet been reported. We report here for the first time the synthesis of a thionitro complex $Co(NSO)Cl_2[P(OPh)_3]_2$.

Experimental Section

All the reagents used were analytical or chemical pure grade. All the solvents were dried and thoroughly degassed before use. Carbon, hydrogen, and nitrogen were analyzed by the Microanalytical Laboratory of Indian Institute of Technology, Kanpur, India. The analyses for chloride and cobalt were carried out by standard methods.[5]

For the phosphorus estimation the sample was decomposed with sodium peroxide, sugar, and sodium nitrate in the ratio 20:1:3 in a Parr-Bomb crucible, and the mass was extracted with water. A few milliliters of concentrated sulfuric acid was added to the water extract which was then heated until SO_3 fumes were evolved. It was diluted with water and filtered if necessary. Phosphorus in this solution was estimated as phosphorus ammonium molybdate.

The infrared spectra were recorded as CsI pellets with a Perkin-Elmer model 580 infrared grating spectrophotometer in the range 4000–250 cm^{-1}. Conductivity measurements were carried out on an Elico conductivity meter type CM-80 using millimolar solutions in nitrobenzene. Magnetic measurements were made with a Gouy balance at room temperature.

A green solution of $(NSCl)_3$[6] (0.08 g) in tetrahydrofuran (15 mL) was slowly added with stirring over about 15 min to a solution of $CoH[P(OPh)_3]_4$[7] (0.40 g) in tetrahydrofuran (20 mL) at 30 °C under pure and dry argon. The stirring was continued for about 30 min more when the solution turned dark green. It was concentrated to 10 mL at room temperature under reduced pressure and filtered under an argon atmosphere. On addition of degassed petroleum ether to the filtrate, a green complex precipitated out. The solid was washed with water and dried in air whereby its color changed from green to yellowish green. The yellowish green complex $Co(NSO)Cl_2[P(OPh)_3]_2$ (I) (mp 118 °C) thus obtained was analyzed (yield, 0.107 g; 43%).

Anal. Calcd for $Co(NSO)Cl_2[P(OPh)_3]_2$: C, 53.4; H, 3.7; N, 1.7; P, 7.6; Co, 7.1; S, 3.9; Cl, 8.8. Found: C, 53.5; H, 3.8; N, 1.6; P, 7.7; Co, 7.0; S, 4.1; Cl, 9.0.

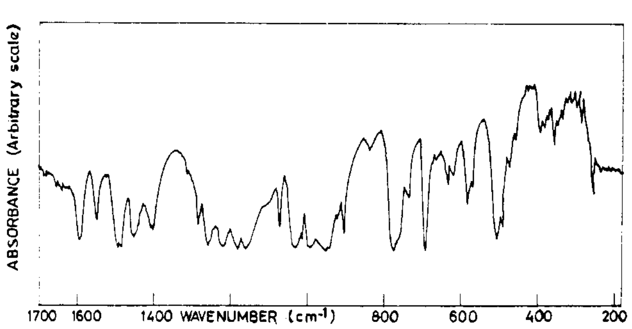

Figure 1. Infrared spectrum of $Co(NSO)Cl_2[P(OPh)_3]_2$.

The solution obtained in the above washings was concentrated on a waterbath to about 10 mL. On cooling, bright yellow needles of S_4N_4 were separated out.

Results and Discussion

Dichlorothionitrobis(triphenyl phosphito)cobalt(III) is a yellowish green, diamagnetic solid that dissolves in dichloromethane, chloroform, and benzene and is insoluble in ether. The compound is reasonably stable in air but is best stored under an inert atmosphere. Its molecular weight was found to be 772. Its conductivity data (6 Ω^{-1} cm^2 mol^{-1}) rules out the ionic character of the compound.

Its IR spectrum in CsI exhibited absorption bands at 1540 and 990 cm^{-1} besides the characteristic bands of triphenylphosphite. The band at 1540 cm^{-1} is assigned to $\nu(NO)$ since the band due to $\nu(NS)$ should not appear at such a high wave number (e.g., the NS triple bond of NSF absorbs at only 1372 cm^{-1}). The peak at 990 cm^{-1} is asigned to $\nu(NS)$.

The IR spectrum of the green solution obtained after the addition of $(NSCl)_3$ to $CoH[P(OPh)_3]_4$ exhibited a band at 1130 cm^{-1} together with weak bands at 1540 and 990 cm^{-1}. The 1130-cm^{-1} band is assigned to $\nu(NS)$.[8] This band disappears on exposing the solution to oxygen or air. It has been concluded that the green solution is a mixture of thionitrosyl and thionitro complexes, which on further exposure to air or oxygen were converted to pure thionitro complex. Presumably, first a five-coordinated air-sensitive intermediate thionitrosyl complex $Co(NS)Cl_2[P(OPh)_3]_2$ ($\nu(NS)$ = 1130 cm^{-1}) was formed which in the presence of air or oxygen was oxidized to a thionitro complex:

$$\mathrm{CoH[P(OPh)_3]_4 + (NSCl)_3 \xrightarrow[-2P(OPh)_3]{THF/30\ {}^\circ C} Co(NS)Cl_2[P(OPh)_3]_2 + H^+ + Cl^- + 2NS}$$

$$\mathrm{2NS \rightarrow {}^1/_2S_4N_4}$$

$$\mathrm{Co(NS)Cl_2[P(OPh)_3]_2 + {}^1/_2O_2 \rightarrow \underset{I}{Co(NSO)Cl_2[P(OPh)_3]_2}}$$

In transition-metal thionitrosyl complexes the thionitrosyl group is generally coordinated through the nitrogen atom of the NS group.[8] This has been supported by the fact that in the thionitrosyl group (N^{δ}–$S^{\delta+}$) the nitrogen end is negatively charged and the sulfur end is positively charged.[9] Therefore, it is presumed that in the cobalt thionitrosyl complex $Co(NS)Cl_2[P(OPh)_3]_2$ the thionitrosyl group is coordinated

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(1) Clarkson, S. G.; Basolo, F. *Inorg. Chem.* **1973**, *12*, 1528.

(2) Ashmore, P. G.; Burnett, M. G.; Taylor, B. J. *Trans. Faraday Soc.* **1962**, *80*, 685.

(3) Tamaki, M.; Masuda, I.; Sinra, K. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 171.

(4) Trogler, W. C.; Marzilli, L. G. *Inorg. Chem.* **1974**, *13*, 1008.

(5) Vogel, A. I. "Text-book of Quantitative Inorganic Analysis", 3rd ed.; Longmans, Green and Co.: London, 1961.

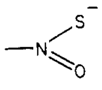
(6) Jolly, W. L.; Maguire, K. D. *Inorg. Synth.* **1967**, *9*, 102.

(7) Levison, J. J.; Robinson, S. D. *J. Chem. Soc. A* **1970**, 96.

(8) Bishop, M. W.; Chatt, J.; Dilworth, J. R. *J. Chem. Soc., Dalton Trans.* **1979**, *1*. Kolthamer, B. W. S.; Legzdins, P. *J. Am. Chem. Soc.* **1978**, *100*, 2247. Pandey, K. K.; Datta, S.; Agarwala, U. C. *Z. Anorg. Allg. Chem.* **1980**, *468*, 228. Jain, K. C.; Pandey, K. K.; Katiyar, S. S.; Agarwala, U. C. *Proc. Int. Conf. Coord. Chem. 21st* **1980**, 440: Pandey, K. K.; Agarwala, U. C. *Inorg. Chem.* **1981**, 20, 1308; *Indian J. Chem.* **1981**, *20*, 74.

(9) Salahub, D. R.; Messmer, R. P. *J. Chem. Phys.* **1976**, *64*, 2039.

through the nitrogen atom (Co–NS) and not through the sulfur atom. The oxidation of the Co–NS moiety with oxygen may lead to the formation of two possible products $CoNSO^-$ (linear thiazate) or $CoN(O)S^-$ (thionitro), which could be distinguished by IR spectrum.[10] Thus the bands due to asymmetric, symmetric stretching, and bending modes of the coordinated thiazate group (NSO^-) appear at 1160, 1060, and 565 cm^{-1}, respectively, and those of thiazate ion (linear NSO^- group) at 1270, 990, and 515 cm^{-1}, respectively. It is therefore presumed that the ligand NSO^- in the cobalt complex is bonded not as thiazate but in the thionitro



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form. The far-IR spectrum of (I) showed two bands at 355 and 390 cm^{-1} assigned to ν(Co–Cl).

The complex was prepared a number of times. In each case the melting point of the compound was found in the range ±2 °C. Under the experimental conditions the possibility of formation of a mixture of many geometrical isomers exists. However, the consistancy of the product suggests that it is one of the many possible isomers.

The reduction of trithiazyl trichloride to tetrasulfur tetranitride by iron[11] and copper[12] has been reported recently, but no one has used a complex for the reduction of $(NSCl)_3$. This novel route for the preparation of S_4N_4 is of importance since it is one of the most valuable starting materials for preparing other inorganic sulfur–nitrogen compounds.

Registry No. I, 80028-18-8; $(NSCl)_3$, 5964-00-1; $CoH[P(OPh)_3]_4$, 41089-90-1.

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(10) Armitage, D. A.; Brand, J. C. *J. Chem. Soc., Chem. Commun.* **1979**, 1078. Pandey, K. K.; Agarwala, U. C. *Indian J. Chem.* **1981**, *20*, 906.

(11) Banister, A. J.; Fielder, A. J.; Hey, R. G.; Smith, N. R. M. *J. Chem. Soc., Dalton. Trans.* **1980**, 1457.

(12) Berthen, M. P.; Vinneht, H.; Monteil, Y. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *35*, 329.

Contribution from the Gibbs Chemical Laboratories,
Harvard University, Cambridge, Massachusetts 02138,
and the Department of Chemistry, Brandeis University,
Waltham, Massachusetts 02154

Boron Hydride Valence Structures. A Topological Approach

W. N. Lipscomb* and I. R. Epstein

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We wish to correct two labeling errors in our previously published paper[1] having the above title and to make two additions, prompted by recent interest[2,3] in these topological three-center bond structures.

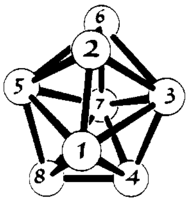

Figure 1. Numbering system for $B_8H_8^{2-}$ valence structures.

For B_6H_{10} the doubly degenerate valence structure should be labeled as 1–2,2–6. For hypothetical $B_8H_8^{2-}$ of D_{4d} symmetry, the labeling should read 1–2,1–5,5–8. These errors arose from translation of the numbering system used in the computer program into the conventional numbering system of the publication.[1] The computer program itself produced correct results, and in particular yielded correctly both the number and the topology of these valence structures.

The first addition is the list of two-center, three-center valence structures for B_8H_8 of D_{2d} symmetry, which is connected as shown in Figure 1. We list here the type (a–e), two-center bonds, and number of equivalent structures (in parentheses) as follows: a, 12,47,48 (4); b, 12,48,67 (2); c, 12,48,78 (4); d, 23,26,56 (2); e 25,26,36 (2). Thus, there are 14 valence structures.

The second addition concerns $B_{12}H_{12}^{2-}$, for which we refer the reader to the publication by Gielen.[2] Our program has selected 240 structures as follows: 20 of type 27_b^+, 20 of type 27_b^- (both of C_3 symmetry); 60 of type 31^+, 60 of type 31^- (both of C_1 symmetry); 20 of type 39 (of C_{3v} symmetry); and 30 of type 40^+, 30 of type 40^- (both of C_2 symmetry). Gielen's paper contains a complete specification of the two-center and three-center bonds in these valence structures. Thus, our 240 structures correct the 5430 structures proposed by Gielen[2] and the 132 structures of an incomplete study supplied by us at the request of Aihara.[3] Finally, in all of our valence structures the specification of locations of single bonds is sufficient to establish uniquely the positions of three-center bonds.

Acknowledgment. We thank the National Science Foundation, Grant No. CHE77-19899, for support and acknowledge the questions that were raised by M. Gielen, which led us to these corrections and additions.

Registry No. $B_8H_8^{2-}$, 12430-13-6; $B_{12}H_{12}^{2-}$, 12356-13-7.

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* To whom correspondence should be addressed at Harvard University.

(1) I. R. Epstein and W. N. Lipscomb, *Inorg. Chem.*, **10**, 1921 (1971).

(2) M. Gielen, *Bull. Soc. Chim. Belg.*, **90**, 501 (1981).

(3) J. Aihara, *J. Am. Chem. Soc.*, **100**, 3339 (1978).

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