Table I

Experimental Transpiration Data

Temp., °K.	Flow rate, cc./min. (STP)	Weight loss/ unit vol., mg./cc. × 10^3
878	6.5	6.18
	7.5	6.11
	8.4	6.35
916	6.23	6.96
	7.16	7.10
	7.77	6.84
948	7.16	11.59
	7.77	10.72
	8.52	11.25
1003	4.69	8.79
	5.37	8.76
	6.05	8.61
	6.54	8.73

tion of volatile products in a side reaction, like silicon oxyfluorides. Careful checks showed no appreciable weight losses of the reaction vessel. Ehlert[6] also studied the mass spectra of species produced in the reaction of CaF_2 with Si + SiO_2 and found silicon oxyfluorides to be of minor importance (<1%).

Conclusions

In the light of the synthesis of SiF_2 and $(SiF_2)_x$,[2,3] various gaseous polymers were considered in attempted calculations of equilibrium constants from the experimental results and available thermodynamic data. The general equilibrium constant at a given temperature for forming $(SiF_2)_x(g)$ is

$$K_x{}^T = \frac{P_{(\mathrm{SiF}_2)_x}}{(P_{\mathrm{SiF}_4})^{x/2}}$$

For forming gaseous perfluorosilanes (Si_xF_{2x+2}), the general equilibrium constant is

$$K_x{}^T = \frac{P_{\mathrm{Si}_x\mathrm{F}_{2x+2}}}{(P_{\mathrm{SiF}_4})^{(x+1)/2}}$$

By varying the SiF_4 partial pressure one can learn something about the true formulas of the gaseous molecule. In particular, from the fact that the weight losses go from being easily measurable at ~1 atm. SiF_4 to being undetectable at 90 mm SiF_4 pressure, one concludes that the SiF_4 dependence is definitely not one-half or first power, which eliminates the polymers $(SiF_2)_{x=1-2}$. Further, if SiF_2 monomer is assumed, the weight losses for the 720–740 mm. SiF_4 experiments lead to an apparent heat of formation of −163 kcal. mole^{-1}, which is far too stable. If $(SiF_2)_2(g)$ were assumed to be the major species, one would require a SiF_2 dimerization energy not too different from that for CF_2 and there is no other evidence for this. Thus, the work reported here suggests the gaseous species is either $(SiF_2)_x$, where $x \geq 3$, or Si_xF_{2x+2}, where $x \geq 2$.

Qualitative molecular orbital arguments, of the type recently presented by Peters,[10] would support the existence of a stable SiF_2– polymer, possibly cyclotetraperfluorosilylene. Mass spectrometric and gas chromatographic studies of low-temperature pyrolysis products from solid SiF_2 polymers[11] indicate that $Si_2F_6(g)$ and other perfluorosilanes can be formed. If the major product of this reaction is assumed to be $Si_2F_6(g)$, one finds the heat of formation of $Si_2F_6(g)$ to be −565 ± 10 kcal./mole. This corresponds to a Si–Si bond energy of 45 ± 10 kcal./mole, while the recent study of Gunn and Green[12] on Si_2H_6 indicated about 63 kcal./mole for the Si–Si interaction. The weaker bond in the perfluoro compound is consistent with other experimental data on similar systems, *e.g.*, C_2H_4 and C_2F_4, C_2H_6 and C_2F_6, etc.[13]

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Metal Nitrosyls. IV. On the Red and Black Isomers of Cobalt Nitrosopentaammines[1]

By Robert D. Feltham

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The earliest example of the isomerism of a compound containing a single NO group is that of the red and the black cobalt compounds $[Co(NH_3)_5NO]X_2$. The earlier literature has been summarized elsewhere.[2–4]

In general, previous workers considered one isomer to be a monomer and the other to be a dimer, the dimer usually being referred to as a hyponitrite, but disagreement has existed over whether the red or the black isomer is the dimer. The problem then is to determine which isomer is, in fact, the dimer (or monomer). Since the red isomer is the more stable of the two, it was chosen for investigation.

Experimental

The red compound $[Co(NH_3)_5NO][NO_3]_2 \cdot 0.5H_2O$ was prepared according to the method of Werner and Karrer.[5] A solution of 30.5 g. of $Co(NO_3)_2 \cdot 6H_2O$ in 50 ml. of distilled water was cooled in an ice bath and 150 ml. of concentrated ammonium hydroxide was slowly added. The solution was filtered and nitric oxide was then passed into the solution for 3–4 hr. The brick-red product was filtered and washed with ethanol, then with ether, and finally dried under vacuum. *Anal.*[6] Calcd. for $[Co(NH_3)_5NO][NO_3]_2 \cdot 0.5H_2O$: H, 5.25; Co, 19.2; NH_3, 27.8; N, 36.5. Found: H, 5.63; Co, 19.3; NH_3, 28.0; N, 36.3.

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[1] This research was sponsored by The International Nickel Company, Inc.

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[6] The elemental analyses were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

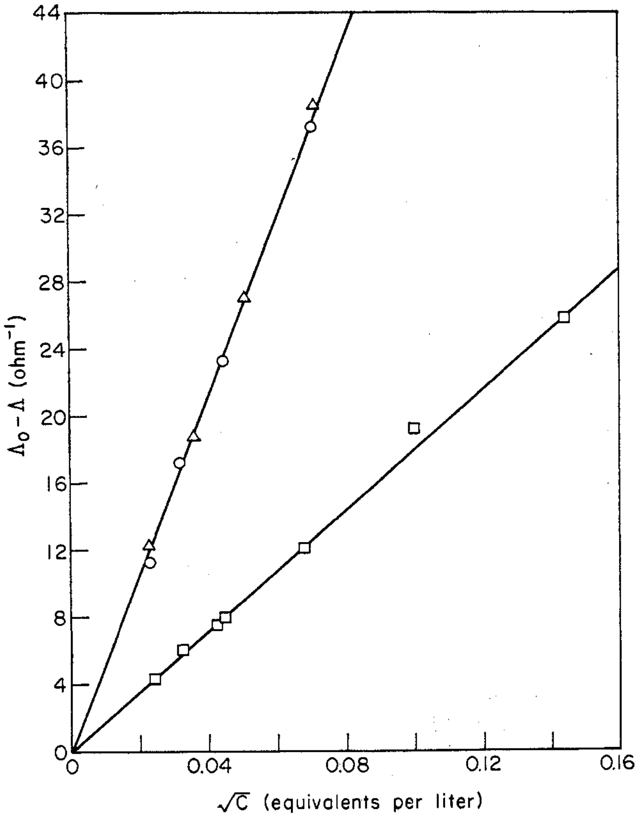

Fig. 1.—The equivalent conductivity of $[Co(NH_3)_5NO][NO_3]_2\cdot 0.5H_2O$, Δ; of $K_4Fe(CN)_6$, O; and of $(Co(NH_3)_5NO_2)Cl_2$, □.

The infrared frequencies are: 3300 (s), 1630 (m), 1490 (w), 1350 (vs), 1135 (m), 1050 (m), 930 (m), 850 (m), 820 (m), and 720 (w). The infrared spectrum of the compound was measured in Nujol and halocarbon mulls on a Beckman IR-9 spectrophotometer. The conductivity of the compound was measured as a function of concentration in nitrogen-purged distilled water using an Industrial Instruments, Inc., Model 16B2 conductivity bridge.

Results

The conductivity of the red cobalt nitrosopentaammine compound, along with that of $K_4Fe(CN)_6$[7] and $Co(NH_3)_5NO_2Cl_2$,[8] is shown in Fig. 1. This graphical method for presenting the conductivity data has been found to be most advantageous.[9] It consists of extrapolating the conductivity to infinite dilution to obtain Λ_0, and then plotting the data as a function of $\Lambda_0 - \Lambda$. In this way a large variety of ion types can be compared on a single graph.

The slope, $\Lambda_0 - \Lambda/\sqrt{C}$, is a function of the electrolyte type and, as can be seen from Fig. 1, clearly distinguishes between 2:1 and 4:1 electrolytes. The fact that the slope of the red isomer is identical with that of $K_4Fe(CN)_6$ unequivocally establishes the red isomer as a 4:1 electrolyte.

Discussion

The fact that the red isomer is a 4:1 electrolyte identifies it as the dimer, as was originally postulated by Werner.[5] These results are in agreement with the ionic weight of the red isomer measured by Brintzinger.[10] He found an ionic weight of 380 (*vs.* 348 calcd. for the dimer) for the red cobalt pentaammine. These results were also confirmed by recent ion-exchange measurements.[11]

The way in which the complex dimerizes cannot be decided on the basis of the conductivity measurements. The polarographic measurements indicate that the cobalt atom in the red isomer is similar to complexes of the type $Co(NH_3)_5Cl^{2+}$, and should be formulated as a dimeric Co(III) pentaammine complex. The absorption at 1050 cm.$^{-1}$ in the infrared spectrum occurs in the same region in which the hyponitrite ion absorbs.[12] It is therefore concluded that the red isomer is the cobalt(III) pentaammine hyponitrite, $[(NH_3)_5CoON{=}NOCo(NH_3)_5]^{4+}$.

It was not possible to measure the conductivity of the black isomer because of its instability. However, it must be the monomeric nitrosyl. This agrees with the conclusion of Bertin[3] that the black isomer is a nitrosyl with the nitrosyl frequency at 1620 cm.$^{-1}$. Although not pointed out by the authors in ref. 3, this frequency is in good agreement with the nitrosyl frequency found for $[(CH_3)_2NCS_2]_2NOCo$.[13]

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N-Methylpyridinium Triiodotetracarbonylmetallates of Molybdenum and Tungsten

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The anion $[Cr(CO)_5I]^-$ has been oxidized to neutral $Cr(CO)_5I$ by treatment with certain oxidizing agents such as triiodide ion, ferric ion, and aqueous hydrogen peroxide.[1] It seemed of interest to investigate oxidation of the analogous molybdenum and tungsten derivatives $[M(CO)_5I]^-$,[2] readily available as their N-methylpyridinium salts, in order to prepare neutral carbonyl iodide derivatives of these metals.

Studies on the iodine oxidation of the salts $[C_5H_5NCH_3][M(CO)_5I]$ (M = Mo or W) have instead led to the unexpected discovery of the interesting derivatives $[C_5H_5NCH_3][M(CO)_4I_3]$ described in this note.

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[2] M refers to molybdenum and tungsten.