can be bounded for nitration by finding structures possessing sufficient hindrance so that proton transfer is the rate-determining step.

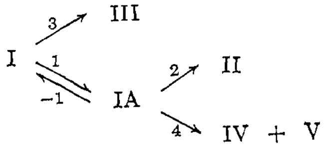
The explanation advanced to account for the formation of 2,4-dinitro-3,5-di-*t*-butyltoluene (IV) and 2,6-dinitro-3,5-di-*t*-butyltoluene (V) in addition to 1,3-dinitro-2,4,6-tri-*t*-butylbenzene (II) and 1,2-dinitro-3,5-di-*t*-butylbenzene (III) upon nitration of 2,4,6-tri-*t*-butylnitrobenzene (I) requires that proton loss from the intermediate cyclohexadienyl cation (Ia) be competitive with molecular rearrangement.[4] Barring an unusual transition state for proton loss from Ia, a partitioning isotope effect (change in product distribution) is required regardless of the over-all rate-determining step. However, additional considerations imply that, for rearrangement to become competitive with proton loss, the rate of proton loss must be considerably slower than normal. Hence, the possibility exists that the rate of proton loss from Ia may approach being the over-all rate-determining step in the formation of II. We report here experimental verification of both the requirement and the possibility.

The distribution of products upon nitration of I and I-3,5-d_2 are given in Table I. These data were obtained by chromatographic analyses (Aerograph A-90P3 SE 30, $^1/_4$ in. × 6 ft, 220°, 100 ml min^{-1}) and were found to be reproducible to within ±1%.

Table I. Product Distribution in Nitration of 2,4,6-Tri-*t*-butylnitrobenzene and 2,4,6-Tri-*t*-butylnitrobenzene-3,5-d_2

Conditions	Reactant	Products, % II	III	IV	V	$(k_H/k_D)_{II/IV}$	$(k_H/k_D)_{II/III}$
HNO_3 (90%), 0°	I	58.9	4.6	34.3	2.2	3.1	2.5
	I-d_2	32.2	6.4	58.3	3.1		
HNO_3–H_2SO_4 in CH_3NO_2 at 40°	I	81.8	3.5	13.7	1.0	3.0	2.7
	I-d_2	60.4	7.0	30.2	2.4		

Assuming the reaction scheme shown, the product ratios, $(II/IV)_H(IV/II)_D$, lead directly to the partitioning isotope effect, $(k_H/k_D)_{II/IV}$.[5] That this isotope effect is larger than the corresponding partitioning isotope effect, $(k_H/k_D)_{II/III}$, indicates that step 1 has some kinetic importance. That is, the combined velocities of steps 2 and 4 are not too much slower than the velocity of step −1. Calculations based on present data indicate that v_{-1}/v_2 is equal to *ca.* 5. Further confirmation of this conclusion is obtained from direct kinetic studies. First-order rate constants for the disappearance of I and I-3,5-d_2 in nitromethane solution containing nitric acid (10.8 *M*) and sulfuric acid (0.47 *M*) at 40° were found to be 2.91 × 10^{-5} and 1.65 × 10^{-5} sec^{-1}, $(k_H/k_D)_{kinetic}$ = 1.8. The calculated observed kinetic isotope effect based on product distribution data is 2.2.



Nitration of I yielding II is the first known aromatic nitration exhibiting a primary kinetic isotope effect.[6] Its occurence is in harmony with prediction. Within present error limits, the isotope effect data corroborate the reaction scheme proposed to account for the products of nitration of I.

Acknowledgment. It is a pleasure to acknowledge the technical assistance of Linda James.

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[4] P. C. Myhre and M. Beug, *J. Am. Chem. Soc.*, **88**, 1568 (1966).

[5] The assumption is implicit in this treatment that the only step sensitive to deuterium substitution is hydrogen loss from Ia yielding II.

[6] Numerous investigations of kinetic isotope effects in nitration have been conducted since the classic work of L. Melander, *Arkiv Kemi*, **2**, 211 (1950). Careful reviews and tabulations of these data have been made recently by E. Berliner, *Progr. Phys. Org. Chem.*, **2**, 157 (1964); H. Zollinger, *Advan. Phys. Org. Chem.*, **2**, 163 (1964).

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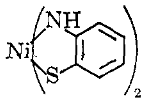
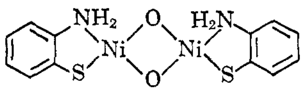
So-called Planar, Low-Spin Bis(*o*-aminobenzenethiol)cobalt(II)

Sir:

The recent suggestion[1] that the dark blue nickel complex of *o*-aminobenzenethiol should be formulated as I rather than II has prompted us to report work on some complexes of this ligand: $M^{II}(SC_6H_4NH_2)_2$, M = VO (lime green, μ_{eff} = 1.77 BM at room temperature), Cr (light blue, μ_{eff} = 4.7 BM), Mn (pale cream, μ_{eff} = 5.55 BM), Fe (pale yellow, μ_{eff} = 3.90 BM), Co (orange-brown, μ_{eff} = 4.10 BM), Ni (yellow, diamagnetic), and Zn (white, diamagnetic); $Co(SC_6H_4NH_2)_3$ (dark green, μ_{eff} = 0.5 BM); and $Cu(SC_6H_4NH_2)$ (cream, diamagnetic). The first five compounds are new and are air-sensitive. Analytical data are summarized in Table I.



I



II

The dark blue nickel compound is prepared by oxidation of yellow $Ni^{II}(SC_6H_4NH_2)_2$ in alkaline conditions.[2] Our analytical data show no oxygen to be present and so agree with I, not with the older oxygen-bridged formulation II.[2]

The cobalt(II) complex of *o*-aminobenzenethiol was reported by Livingstone[3] to be dark blue with a magnetic moment of 2.6 BM at room temperature. It has been considered a typical low-spin, planar cobalt(II) complex.[4-6] It was prepared[3] by boiling in suspension in acetone the orange-brown precipitate which ap-

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[1] E. I. Stiefel, J. H. Waters, E. Billig, and H. B. Gray, *J. Am. Chem. Soc.*, **87**, 3016 (1965).

[2] W. Hieber and R. Bruck, *Z. Anorg. Allgem. Chem.*, **269**, 13 (1952).

[3] S. E. Livingstone, *J. Chem. Soc.*, 1042 (1956).

[4] B. N. Figgis and R. S. Nyholm, *ibid.*, 338 (1959).

[5] D. H. Busch, "Cobalt," ACS Monograph 149, R. S. Young, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, Chapter 6.

[6] C. M. Harris and S. E. Livingstone, "Chelating Agents and Metal Chelates," F. P. Dwyer and D. P. Mellor, Ed., Academic Press Inc., New York, N. Y., 1964, p 126.

Table I. Analyses of *o*-Aminobenzenethiol Complexes

Compound[a]	% metal		% C		% H		% N		% O	
	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd
$VO(SC_6H_4NH_2)_2$	16.11	16.15	45.82	45.71	3.91	3.84	8.76	8.88	4.93	5.07
$Cr(SC_6H_4NH_2)_2$	...	...	48.14	48.00	3.95	4.03	9.35	9.33	...	...
$Mn(SC_6H_4NH_2)_2$	18.04	18.12	47.51	47.54	4.11	3.99	8.99	9.24	...	...
$Fe(SC_6H_4NH_2)_2$	18.35	18.35	47.19	47.39	4.12	3.98	9.04	9.21	...	...
$Co(SC_6H_4NH_2)_2$[b]	19.18	19.19	46.84	46.92	4.03	3.94	9.06	9.12	...	...
	18.91	...	46.87	...	3.85	...	9.28	...	...	...
$Co(SC_6H_4NH_2)_3$	13.59	13.66	50.04	50.13	4.17	4.20	9.68	9.74	...	...
"$Co(SC_6H_4NH_2)_2OH$"[b]	17.88	18.18	44.26	44.46	4.02	4.04	8.63	8.64	4.87	4.94
	17.96	...	44.66	...	3.99	...	8.56	...	5.40	...
$Ni(SC_6H_4NH_2)_2$	19.12	19.13	45.93	46.96	3.72	3.94	9.53	9.13	...	...
	...	...	47.16[c]	...	3.91[c]	...	...	...	...	...
$Ni(SC_6H_4NH)_2$[d]			47.23		3.51				1.12	
	19.16	19.25	47.70[c]	47.26	2.97[c]	3.30	8.78	9.18	0.78[c]	0
			47.50[e]		3.14[e]		8.39[e]		0.69[e]	
$Cu(SC_6H_4NH_2)$	33.86	33.86	38.52	38.39	3.21	3.22	7.27	7.46	...	...
$Zn(SC_6H_4NH_2)_2$	20.77	20.84	...	...	...	...	...	...	...	...

[a] O, C, H, and N microanalyses were performed by A. Bernhardt, Max Planck Institut, Mulheim, Germany. [b] Analyses are from different preparations. [c] Duplicate analyses. [d] Sample was recrystallized from benzene. The other compounds could not be recrystallized because of poor solubility; nevertheless, the analytical figures are satisfactory throughout. [e] Unrecrystallized sample, different preparation from *d*.

peared when the ligand was added to cobalt acetate in hot aqueous alcohol. We have found that the orange-brown compound, prepared in the absence of air, is the true cobalt(II) complex $Co(SC_6H_4NH_2)_2$. It has a room temperature magnetic moment of 4.1 BM, *i.e.*, is high spin, and the moment is in the range expected for tetrahedral cobalt(II). However, the plot of reciprocal susceptibility *vs.* temperature shows departures from linearity at the lower temperatures, and extrapolation of the linear, higher temperature, part of the curve gives a large value of 53° for θ, the Curie–Weiss constant. Since this antiferromagnetic behavior could be due to interactions between the metal atoms in a sulfur-bridged structure, the magnetic moment is not immediately diagnostic of stereochemistry. The iron(II) compound is antiferromagnetic with a Neel point at 138°K. The original cobalt results suggested that *o*-aminobenzenethiol should be classified as a high-field ligand. However, in all complexes where states of different multiplicity are possible, high-spin complexes are formed, except with nickel(II).

As shown in Table I reproducible analytical data, including oxygen analyses, indicate empirical formulation of the blue substance as $Co(SC_6H_4NH_2)_2OH$ or $Co(SC_6H_4NH_2)_2O$, although its color and magnetic moment ($\mu_{\text{eff}} = 2.7$ BM, $\theta = 16°$) are consistent with formulation analogous to I. Similar moments and θ values have been reported before.[3,4] The blue substance and the compounds listed above show composite infrared absorptions arising from the NH_2 stretching modes, whereas with the blue nickel compound, and with the similar blue compound $Ni(NHC_6H_4NH)_2$, a single, sharp and strong NH absorption is found.[7] In addition, the blue substance has a broad absorption at 3500 cm^{-1} which would seem to indicate a hydroxo species.

However, aerial oxidation in other conditions, *e.g.*, acetone or aqueous alkali at room temperature, gave paramagnetic blue materials with unreproducible analyses. Furthermore, aerial oxidation in aqueous ammoniacal solution gave the dark green compound $Co(SC_6H_4NH_2)_3$. This has previously been reported[2] but could not be obtained by the published method. Analytical data are given in Table I; only metal analyses were previously reported. The compound is essentially diamagnetic. Its infrared spectrum, except for the absence of an OH absorption, and its reflectance spectrum are identical with those of the blue compound. Their X-ray powder photographs are almost identical. Thus we believe that the so-called blue cobalt(II) complex is not a true compound, but a mixture of the cobalt(III) compound $Co(SC_6H_4NH_2)_3$ and some black, paramagnetic, and very finely divided cobalt oxide or hydroxide species. The aerial oxidation in boiling acetone is apparently accompanied by ligand transfer to produce the tris complex $Co(SC_6H_4NH_2)_3$ and the cobalt oxide or hydroxide species in the appropriate proportions to account for the analytical data.

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(7) D. J. Phillips, unpublished work.

Synthesis and Optical Properties of Bis(toluene-3,4-dithiolato)silicon(IV), -germanium(IV), -tin(IV), and -lead(IV)

Sir:

In this communication are reported the synthesis and partial resolution of a new series of optically active compounds containing as the central atom silicon, germanium, tin, and lead. By reaction of a group IV-A tetrachloride (in the case of lead, the tetracetate) with toluene-3,4-dithiol in an appropriate solvent, a racemic mixture of the enantiomers was prepared.

Partial resolution of the enantiomers was accomplished on a column of activated *d*-quartz. The quartz crystals were activated by boiling in concentrated nitric acid, rinsing with distilled water, and heating in an oven at 110° for at least 3 hr. A column was prepared by placing the dry quartz crystals in a standard 50-ml buret to a height of 30 cm. A saturated solution of each of the compounds in acetonitrile was passed through separate columns and collected in 5-ml increments. These solutions were diluted to a concentration