

complexes of the type  $NiL_4X_2$ , where L and X are ligands widely separated in the spectrochemical series, tetragonal distortion results in a broadening and splitting of the  $\nu_1$  band.<sup>13</sup> The spectra of octahedral complexes such as  $Ni(py)_4Cl_2$ ,  $[Ni(en)_2(H_2O)_2]^{2+}$ , and  $Ni(en)_2(NO_3)_2$  have been explained on the basis of  $\nu_1$  splitting due to tetragonal distortion.<sup>9,14</sup> With the instrumentation available in this study, it was impossible to obtain reflectance absorption measurements in the infrared region from 8000 to 10,000  $cm^{-1}$ . For  $Ni(bipy)_2(NO_3)_2$ , however, the band at 13,500  $cm^{-1}$  is much too high in energy to be attributed to a single  $\nu_1$  band (which is  $10Dq$  for octahedral nickel(II) complexes), unless 4,4'-bipyridine lies considerably higher than pyridine in the spectrochemical series. Therefore, it is assumed that the 13,500- $cm^{-1}$  band is due to a splitting of  $\nu_1$ . Infrared absorption bands for  $Ni(bipy)_2(NO_3)_2$  are typical of monodentate nitrate coordination, and on the basis of stoichiometry and spectral data, a reasonable structure of the complex may be

(13) C. R. Hare and C. J. Ballhausen, *J. Chem. Phys.*, **40**, 792 (1964).(14) M. R. Rosenthal and R. S. Drago, *Inorg. Chem.*, **4**, 840 (1965).

assigned as consisting of Ni(II) ions surrounded octahedrally by four bridging 4,4'-bipyridine molecules and two monodentate coordinated nitrate ions.

Infrared and visible reflectance spectra for  $Co(bipy)_2(NO_3)_2$  and the approximate stoichiometry are consistent with an octahedral structure containing monodentate coordinated nitrate groups. While it is tempting to conclude that the structure is similar to that of  $Ni(bipy)_2(NO_3)_2$ , the impurity of the product based upon analytical data precludes a valid structural assignment. When the product listed as  $Cu(bipy)_2(NO_3)_2$  was dried at 94°, it then analyzed as  $Cu(bipy)(NO_3)_2$ . However,  $Cu(bipy)_2(NO_3)_2$  displayed an absorption maximum at 18,200  $cm^{-1}$  compared to 16,400  $cm^{-1}$  for  $Cu(bipy)(NO_3)_2$ , and assuming that 4,4'-bipyridine is higher in the spectrochemical series than  $NO_3^-$ ,  $CH_3OH$ , or  $H_2O$ , it would seem that the degree of coordination of 4,4'-bipyridine must be higher in the former product than in the latter.

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## Metal Complexes of *o*-Aminobenzenethiol

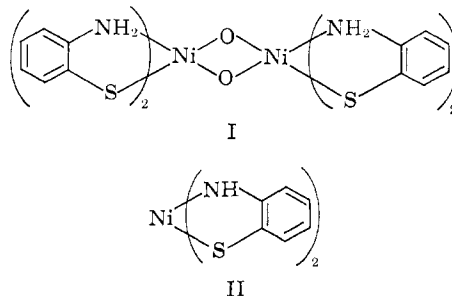
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The compounds  $Zn(abt)_2$ ,  $Cu(abt)$ ,  $Ni(abt)_2$ ,  $Ni(NHC_6H_4S)_2$ ,  $Co(abt)_2$ ,  $Co(abt)_3$ ,  $Fe(abt)_2$ ,  $Mn(abt)_2$ ,  $Cr(abt)_2$ , and  $VO(abt)_2$  ( $abt = o-NH_2C_6H_4S$ ) have been prepared under anaerobic conditions. They have been characterized where possible by solution and reflectance electronic spectra, infrared spectra, X-ray powder photographs, and magnetic studies down to liquid nitrogen temperatures. The original reports of  $Co(abt)_2$  stated that it was a dark blue, low-spin, planar cobalt(II) complex. This dark blue material has been shown to be an oxidation product of the true  $Co(abt)_2$  complex, which is orange-brown and high spin with a sulfur-bridged, six-coordinate structure. The dark blue material has physical properties almost identical with those of the cobalt(III) complex  $Co(abt)_3$  and is a mixture of it and some hydroxide species. In contrast  $Ni(abt)_2$  on oxidation forms the imino complex  $Ni(NHC_6H_4S)_2$ , previously reported as an oxygen-bridged nickel(IV) complex. Presumably as a result of sulfur-bridged structures, several complexes show magnetic interaction, especially  $Fe(abt)_2$  which has a Néel point at 138°K.

There has been considerable recent interest in sulfur ligands, especially those of the dithiol type, which produce series of complexes interrelated by electron-transfer reactions.<sup>1</sup> Some related ligands, including *o*-aminobenzenethiol, have been shown to behave similarly.<sup>2,3</sup> Considerable confusion exists in the literature on the complexes of *o*-aminobenzenethiol, probably owing to their air-sensitive nature. For example, preliminary reports from these<sup>4</sup> and other laboratories<sup>2</sup> showed that the deep blue oxidation product of  $Ni(abt)_2$

( $abt = o-NH_2C_6H_4S$ ) does not have the reported<sup>5</sup> oxygen-bridged structure I but has structure II similar to

(1) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **3**, 814 (1964); E. I. Stiefel, R. Eisenberg, R. C. Rosenberg, and H. B. Gray, *J. Am. Chem. Soc.*, **88**, 2956 (1966).(2) A. L. Balch, F. Röhrscheid, and R. H. Holm, *ibid.*, **87**, 2301 (1965); E. I. Stiefel, J. H. Waters, E. Billig, and H. B. Gray, *ibid.*, **87**, 3016 (1965).(3) R. Röhrscheid, A. L. Balch, and R. H. Holm, *Inorg. Chem.*, **5**, 1542 (1966); A. L. Balch and R. H. Holm, *J. Am. Chem. Soc.*, **88**, 5201 (1966); R. H. Holm, A. L. Balch, A. Davison, A. H. Maki, and T. E. Berry, *ibid.*, **89**, 2866 (1967).(4) L. F. Larkworthy, J. M. Murphy, and D. J. Phillips, *ibid.*, **88**, 1570 (1966). Note, the structural formula cited for  $(abt)_2NiOONi(abt)_2$  in this earlier communication contains a typographical error and it should appear as I in this present paper.(5) W. Hieber and R. Brück, *Z. Anorg. Allgem. Chem.*, **269**, 13 (1952).

that of dithiol complexes. Other reports<sup>6,7</sup> of highly colored complexes of *o*-aminobenzenethiol, in which the colors are now shown to be due to oxidation products, lead us to present a detailed study of the complexes of this ligand, using anaerobic conditions.

### Experimental Section

**Reagents.**—Regent grade *o*-aminobenzenethiol was purified by distillation under nitrogen (2 mm, 76°) and stored under nitrogen. Skin contact was avoided because of the risk of severe dermatitis. Other chemicals used were of AnalaR grade or were purified by standard methods.

**Preparation of the Complexes.**—Analytical data are summarized in Table I. Zn(abt)<sub>2</sub>,<sup>7,8</sup> Ni(abt)<sub>2</sub>,<sup>5,6</sup> and Co(abt)<sub>3</sub><sup>5</sup> have been reported before and Ni(abt)<sub>2</sub> was obtained by the reported procedure<sup>5</sup> but in a nitrogen atmosphere. Ni(NHC<sub>6</sub>H<sub>4</sub>S)<sub>2</sub> was obtained by the procedure reported for "(abt)<sub>2</sub>NiOONi(abt)<sub>2</sub>."<sup>5</sup>

In the subsequent preparations deoxygenated solvents were used and all operations were carried out under nitrogen, unless otherwise stated.

**Mn(abt)<sub>2</sub>.**—A solution of 4.28 ml of *o*-aminobenzenethiol in 50 ml of 75% ethanol was slowly added to a solution of 4.90 g of manganous acetate in 100 ml of 75% ethanol at 45°. The resulting pale cream precipitate was filtered off, washed with 75% ethanol and absolute ethanol, and dried under reduced pressure at about 45°.

The complexes Zn(abt)<sub>2</sub>, Co(abt)<sub>2</sub>, and VO(abt)<sub>2</sub> were obtained similarly from zinc sulfate, cobalt acetate, and vanadyl(IV) sulfate, respectively.

**Fe(abt)<sub>2</sub>.**—To obtain a pure product it was necessary to neutralize with sodium hydroxide the acid liberated during reaction. However, to avoid the formation of hydrated oxides of iron from any slight excess of alkali, a deficiency of sodium hydroxide was used and the remaining acid was neutralized with sodium acetate. Thus a solution of 4.21 ml of *o*-aminobenzenethiol, 1.28 g of sodium hydroxide, and 1.63 g of sodium acetate in 100 ml of 33% ethanol was added slowly to a solution of 5.56 g of ferrous sulfate in 120 ml of 33% ethanol at 35°. After shaking the warm suspension for 40 min, the pale yellow precipitate was filtered off, washed with water, absolute ethanol, and acetone, and dried under reduced pressure at about 40°.

**Cr(abt)<sub>2</sub>.**—A solution of 5.30 ml of *o*-aminobenzenethiol in 50 ml of 50% ethanol was slowly added to a solution of chromous chloride (prepared from 1.35 g of metal) in 40 ml of 50% ethanol. The resulting green suspension was shaken for 40 min and left overnight. The precipitate, which turned blue within 1 hr, was filtered off, washed with 50% ethanol and absolute ethanol, and dried under reduced pressure. The reason for the color change is not known. The low chromium analysis suggests that the complex is contaminated with some excess ligand and possibly a little water. For example, the calculated figures for Cr(NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>S)<sub>2</sub>·0.25(NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>SH) are: C, 48.90; H, 41.7; Cr, 15.70; N, 9.50. The complex was prepared several times under different conditions, but the products always had essentially the same analyses.

**Cu(abt).**—A solution of 3.21 ml of *o*-aminobenzenethiol in 50 ml of 96% ethanol was slowly added to a solution of 2.97 g of cuprous chloride in 225 ml of concentrated ammonia solution. After shaking for 30 min the white precipitate was filtered off and washed with a 9:2 mixture of concentrated ammonia solution and 96% ethanol and then with absolute ethanol. The compound was dried under reduced pressure at about 40°.

**Investigation of Oxidation Products.** Co(abt)<sub>3</sub>.—A solution of 6.00 g of cobaltous chloride, 6.00 g of ammonium chloride in a mixture of 200 ml of concentrated ammonia solution, and 60 ml of

water was added to a solution of 7.8 ml of *o*-aminobenzenethiol in 60 ml of 96% ethanol. The resulting suspension was stirred for 30 min in the air and then filtered. The dark green precipitate was washed with aqueous ammonia, water, ethanol, and ether and then dried under reduced pressure. The published procedure<sup>5</sup> states that this compound can be prepared under nitrogen. However, preparations using this procedure were unsuccessful, and it is difficult to see how the oxidation could occur under these conditions.

**The Substance "Co(abt)<sub>2</sub>OH."**—This dark blue substance was obtained by a modification of the reported procedure.<sup>5</sup> Deoxygenated acetone (250 ml) was added to 2 g of Co(abt)<sub>2</sub> under nitrogen. The brown suspension was then boiled in a large evaporating basin in air for 2 hr. The resulting dark blue solid was filtered off, washed with acetone, and dried under reduced pressure.

**Iron(III) and *o*-Aminobenzenethiol.**—Attempts to prepare a ferric complex by the reaction of *o*-aminobenzenethiol and ferric ammonium sulfate in aqueous ethanol yielded (NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>S)<sub>2</sub> (mp 92°, lit.<sup>8</sup> mp 93°) and ferrous ammonium sulfate. Ferric acetate, chloride, and nitrate were also reduced by excess *o*-aminobenzenethiol. However, in these cases Fe(abt)<sub>2</sub> was first precipitated. This darkened quickly in air.

**Copper and *o*-Aminobenzenethiol.**—Attempts were made to confirm the reported preparation<sup>7</sup> of blue Cu(abt)<sub>2</sub> from direct reaction between cupric salts and *o*-aminobenzenethiol. A slight excess of *o*-aminobenzenethiol was added separately to cupric acetate and cupric nitrate in aqueous ethanol under nitrogen. Reduction to the cuprous state occurred in each case, giving a white precipitate of Cu(abt) and (NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>S)<sub>2</sub>. The mixture darkened in air. Washing the mixture with absolute ethanol yielded a residue of Cu(abt), identified from its analysis and infrared spectrum. Evaporation of the filtrate produced crystals of (NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>S)<sub>2</sub>, identified by its melting point and infrared spectrum. Reduction also occurred using cupric acetate, cupric nitrate, or cupric ammonium chloride, all in ethanolic ammonia.

**Spectra.**<sup>9</sup>—Infrared spectra were obtained from mineral oil mulls using a Grubb-Parsons "Spectromaster" spectrophotometer. Details (cm<sup>-1</sup>) for some compounds are: Co(abt)<sub>2</sub>: 3270 s, 3155 s, 3090 s, 1582 s, 1556 s, 1470 s, 1438 m, 1298 vw, 1267 m, 1210 w, 1168 w, 1160 w, 1088 m, 1062 m, 1035 w, 971 w, 945 w, 928 w, 823 w, 749 s, 735 vs, 680 w, 563 w, 537 m, 486 w, 424 m. "Co(abt)<sub>2</sub>OH": 3485 w, br, 3280 m, 3240 s, 3140 s, 3100 s, 3075 s, 3045 s, 1583 s, 1541 m, 1529 m, 1470 s, 1436 m, 1340 vw, 1296 vw, 1263 w, 1199 w, 1150 w, 1134 m, 1121 s, 1063 w, 1031 m, 938 w, 859 w, 841 vw, 817 w, 761 s, 753 vs, 733 vw, 717 m, 683 m, 648 w, 579 vw, 564 w, 504 vw, 432 m. Co(abt)<sub>3</sub>: identical with the preceding spectrum except for the absence of bands at 3485, 1340, 841, 733, and 579 cm<sup>-1</sup>.

Visible reflectance spectra (30,000–10,000 cm<sup>-1</sup>) were obtained using a Unicam SP 500 spectrophotometer. Air-sensitive samples were enclosed in a sealed silica cell. Visible solution spectra (36,000–11,750 cm<sup>-1</sup>) were obtained using an SP 800 spectrophotometer.

**Magnetic Measurements.**—These were carried out down to liquid nitrogen temperatures by the Gouy method on samples in sealed Pyrex tubes. Measurements were made at different field strengths to check that there was no field dependence. The diamagnetic corrections were calculated from Pascal's constants.

### Results and Discussion

Physical data on the compounds are presented in Tables I–III. Zn(abt)<sub>2</sub>, Ni(abt)<sub>2</sub>, and Co(abt)<sub>3</sub> have been reported before,<sup>5,6,8</sup> the remaining complexes are

(9) The infrared spectra of the other compounds together with the detailed results of magnetic susceptibility measurements have been deposited as Document No. 9996 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and by remitting \$1.25 for photoprints, or \$1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

(6) S. E. Livingstone, *J. Chem. Soc.*, 1042 (1956).

(7) E. J. Olszewski and M. J. Albinak, *J. Inorg. Nucl. Chem.*, **27**, 1431 (1965).

(8) M. T. Bogert and F. D. Snell, *J. Am. Chem. Soc.*, **46**, 1308 (1924); J. Metzger and H. Plank, *Bull. Soc. Chim. France*, 1692 (1956); H. Jadamus, Q. Fernando, and H. Frieser, *J. Am. Chem. Soc.*, **86**, 3056 (1964).

TABLE I  
 ANALYTICAL DATA FOR *o*-AMINOBENZENETHIOL COMPLEXES

Compd <sup>d</sup>	% metal		% C		% H		% N		% O	
	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd
VO(abt) <sub>2</sub> <sup>e</sup>	16.11	16.15	45.82	45.71	3.91	3.84	8.76	8.88	4.93	5.07
Cr(abt) <sub>2</sub> <sup>e</sup>	15.70	17.32	48.14	48.00	3.95	4.03	9.35	9.33	...	...
Mn(abt) <sub>2</sub> <sup>e</sup>	18.04	18.12	47.51	47.54	4.11	3.99	8.99	9.24	...	...
Fe(abt) <sub>2</sub> <sup>e</sup>	18.35	18.35	47.19	47.39	4.12	3.98	9.04	9.21	...	...
Co(abt) <sub>2</sub> <sup>e</sup>	19.18	19.19	46.84	46.92	4.03	3.94	9.06	9.12	...	...
Co(abt) <sub>2</sub>	13.59	13.66	50.04	50.13	4.17	4.20	9.68	9.74	...	...
"Co(abt) <sub>2</sub> OH" <sup>a</sup>	17.88	18.18	44.26	44.46	4.02	4.04	8.63	8.64	4.87	4.9 <sup>d</sup>
	17.96		44.66		3.99		8.56		5.40	
Ni(abt) <sub>2</sub>	19.12	19.13	45.93	46.96	3.72	3.94	9.53	9.13	...	...
			47.16 <sup>b</sup>		3.91 <sup>b</sup>					
Ni(SC <sub>3</sub> H <sub>7</sub> NH) <sub>2</sub>	19.16	19.25	47.70	47.26	2.97	3.30	8.78	9.18	0.78	0
			47.23 <sup>b</sup>		3.51 <sup>b</sup>		...		1.12 <sup>b</sup>	
			47.50 <sup>c</sup>		3.14 <sup>c</sup>		8.39 <sup>c</sup>		0.69 <sup>c</sup>	
Cu(abt) <sub>2</sub> <sup>e</sup>	33.86	33.86	38.52	38.39	3.21	3.22	7.27	7.46	...	...
Zn(abt) <sub>2</sub>	20.77	20.84	...	...	...	...	...	...	...	...

<sup>a</sup> Analyses are from different preparations.    Duplicate analyses.    <sup>c</sup> Different sample.    <sup>d</sup> abt = *o*-NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>S.    <sup>e</sup> New compounds.

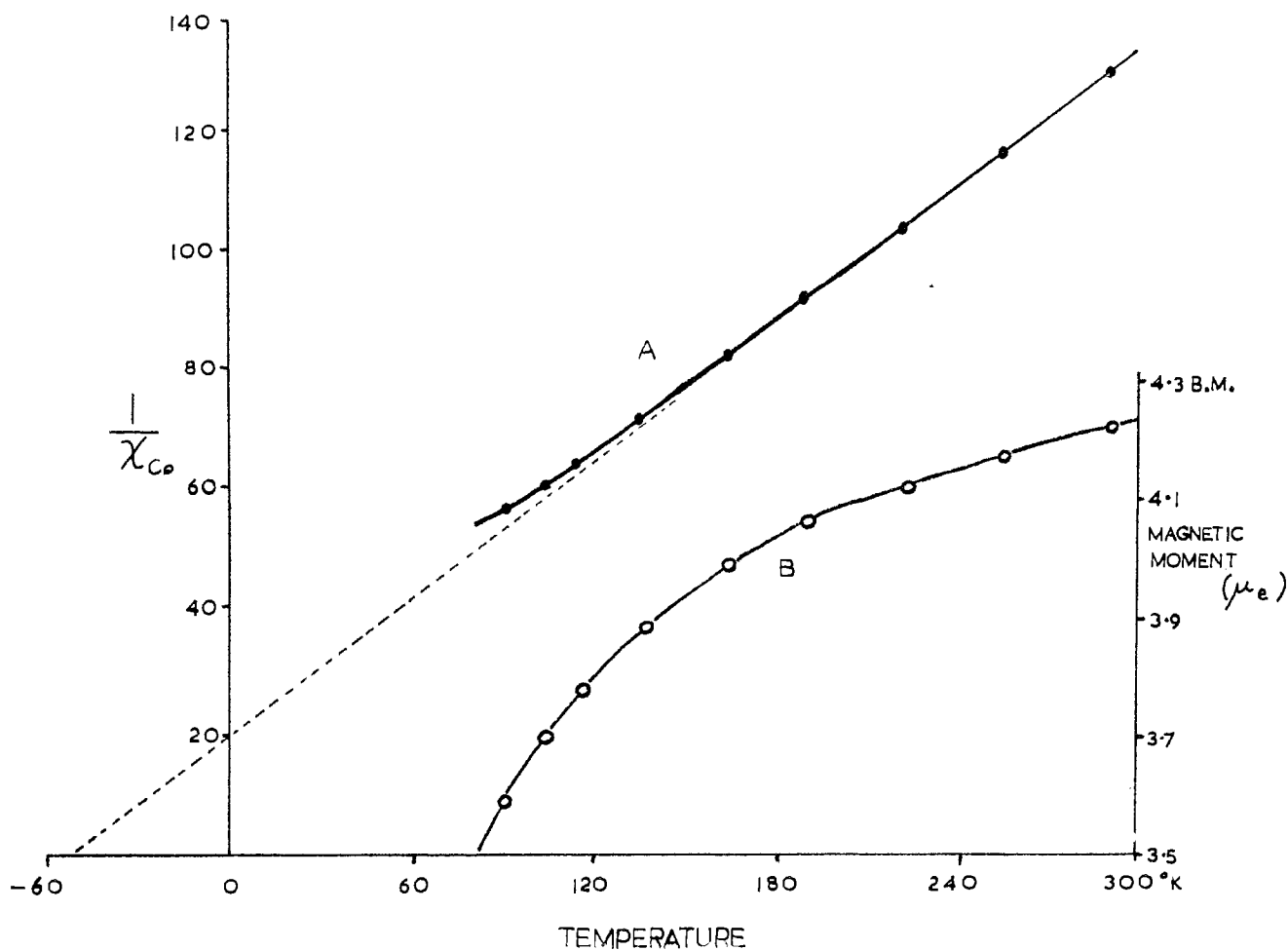


Figure 1.—Temperature dependence of (A) the reciprocal magnetic susceptibility and (B) the magnetic moment of Co(abt)<sub>2</sub>.

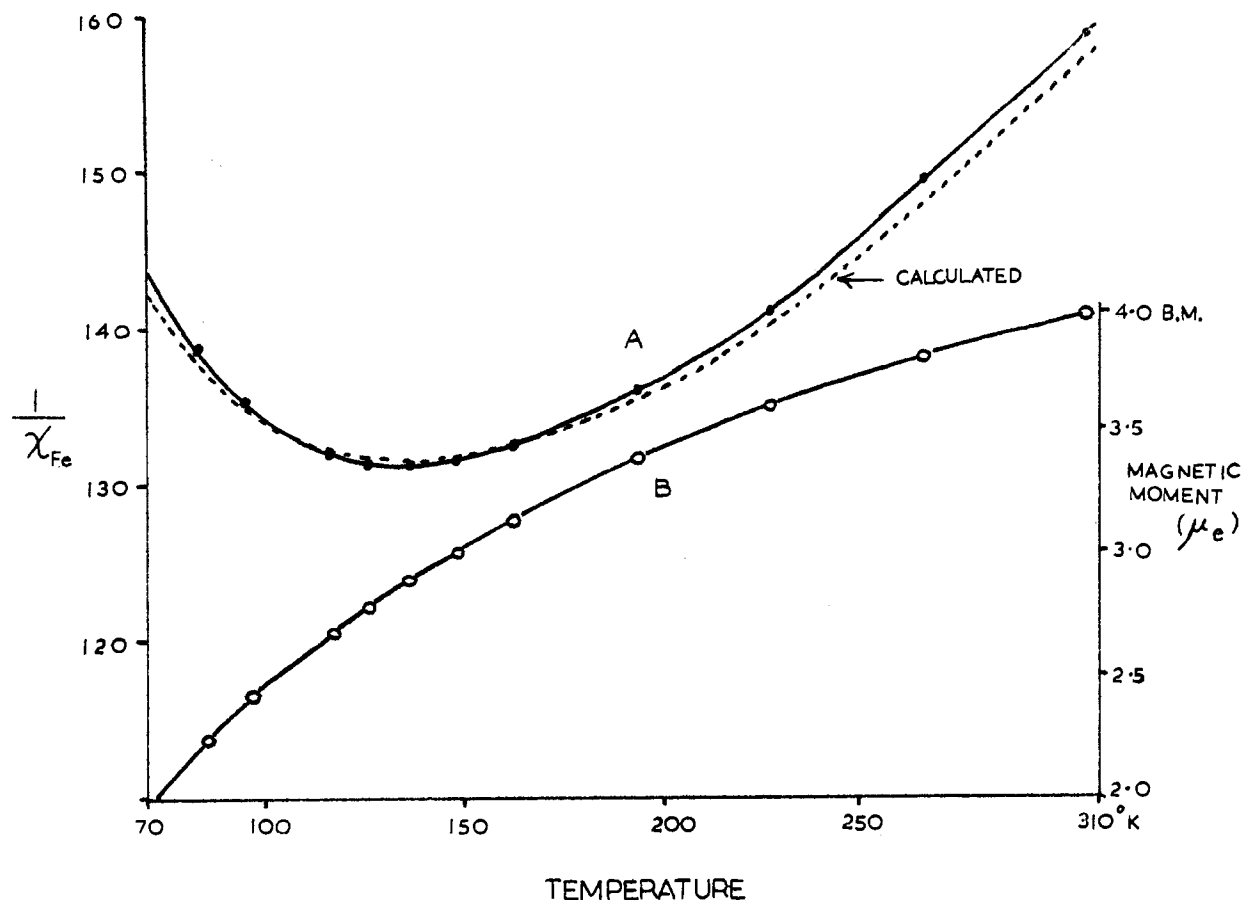
new. Most of the compounds are of the type M<sup>II</sup>(abt)<sub>2</sub> and these are discussed first.

**M<sup>II</sup>(abt)<sub>2</sub> Complexes.**—These are insoluble in most solvents, but very slightly soluble in dimethylformamide (DMF) in which they are nonelectrolytes (Table III). X-Ray powder photographs do not show any cases of isomorphism among these compounds (Table II). The poor solubility of these compounds prevented molecular weight and other measurements in solution and suggests that simple monomeric structures with tetrahedral or planar configurations are unlikely

and that sulfur bridging occurs. The formation of polynuclear species is supported by the magnetic and spectral properties of the complexes.

White Zn(abt)<sub>2</sub> and yellow Ni(abt)<sub>2</sub> are diamagnetic. A single visible absorption in the region of 15,000 cm<sup>-1</sup>, as shown by Ni(abt)<sub>2</sub> (Table III), is usual<sup>10a</sup> for low-spin nickel(II). The suggested six-coordinate structure for this complex must be tetragonally distorted to account for the diamagnetism and this is likely with a bridged system.

Orange-brown Co(abt)<sub>2</sub> has an effective magnetic

Figure 2.—Temperature dependence of (A) the reciprocal magnetic susceptibility and (B) the magnetic moment of Fe(abt)<sub>2</sub>.TABLE II  
X-RAY POWDER PHOTOGRAPH DATA<sup>a</sup>

Compd	<i>d</i> spacings
Zn(abt) <sub>2</sub>	4.59 s, 4.27 vs, 3.57 w, 3.28 vs, 3.00 m, 2.71 vw, 2.55 w, 2.50 w, 2.41 m, 2.31 w, 2.20 w, 2.15 vw, 2.09 w, 2.00 vw, 1.86 vw, 1.82 w, 1.68 w, 1.50 vw, 1.44 vw, 1.35 vw
Ni(abt) <sub>2</sub>	4.54 vs, 3.47 vs, 3.00 s, 2.43 vw, 2.29 vw, 2.15 vw, 2.05 vw, 2.00 vw, 1.85 vw, 1.69 vw
Ni(NHC <sub>6</sub> H <sub>4</sub> S) <sub>2</sub>	4.59 vs, 3.99 s, 3.59 s, 3.35 w, 3.10 m, 2.67 vw, 2.13 vw
Co(abt) <sub>2</sub>	5.48 w, 5.31 s, 4.63 w, 4.50 w, 3.82 m, 3.54 w, 3.04 s, 2.84 w, 2.62 vw, 2.56 vw, 2.30 vw, 2.22 vw, 2.06 w, 1.92 w, 1.83 w, 1.64 vw, 1.47 vw, 1.36 vw
Co(abt) <sub>3</sub>	8.42 m, 6.51 m, 4.86 m, 4.34 vs, 3.83 s
"Co(abt) <sub>2</sub> OH"	8.42 m, 6.47 m, 4.89 m, 4.36 vs, 3.85 s
Fe(abt) <sub>2</sub>	4.49 vs, 3.92 vw, 3.66 m, 3.21 vw, 3.08 s, 2.94 vw, 2.57 vw, 2.41 w, 2.08 m, 1.79 w
Mn(abt) <sub>2</sub>	5.69 s, 4.53 m, 3.79 m, 3.38 w, 3.10 vs, 2.89 w, 2.61 s, 2.34 w, 2.22 m, 2.08 m, 1.94 w, 1.89 vw, 1.84 w, 1.64 w, 1.55 vw, 1.49 vw, 1.40 vw, 1.36 w
Cr(abt) <sub>2</sub>	4.93 w, 4.39 vs, 3.90 m, 3.14 s, 1.89 vw

<sup>a</sup> Obtained using a Philips camera of diameter 5.73 cm and iron-filtered cobalt radiation (1.790-Å wavelength) with samples supported on glass fibers. Oxygen-sensitive samples were coated with diluted collodion.

moment  $\mu_e$  of 4.2 BM at 292°K, near the range usually associated<sup>10</sup> with tetrahedral complexes. However, its magnetic moment diminishes markedly as the temperature is lowered, and although at higher temperatures it obeys the Curie-Weiss law ( $\theta = 53^\circ$ ), below 150°K the reciprocal susceptibility *vs.* temperature plot deviates in a manner characteristic of an antiferromagnetic compound (Figure 1). Since spin-orbit coupling and

TABLE III  
MAGNETIC, ELECTRONIC SPECTRAL, AND CONDUCTANCE DATA

Compd	$10^6 \chi_A$ , cgs units	$\mu_e$ , BM	Temp, °K	$\theta^a$ , °K	Electronic spectra <sup>b</sup> $\nu_{max}$ , $\text{cm}^{-1} \times 10^{-3}$	$\Delta M$ , <sup>c</sup> ohm <sup>-1</sup>
Zn(abt) <sub>2</sub>	-9	0	298	...	...	0.2
Cu(abt)	-5	0	298	...	...	Insol
Ni(abt) <sub>2</sub>	22	0.24	323.5	...	25.4 m, 15.5 s	1.3
Ni(NHC <sub>6</sub> H <sub>4</sub> S) <sub>2</sub>	47	0.35	315	...	11.8 vs, vbr	0.5
Co(abt) <sub>2</sub>	7,574	4.22	292.3	53	20.4 m, 13.7 w 33.3 (18,300), 25.2 (16,100), 16.6 (293)	5.0
"Co(abt) <sub>2</sub> OH"	2,807	2.58	292.8	16	26.5 m, 16.8 s	3.1
Co(abt) <sub>3</sub>	106	0.51	299.2	...	26.0 m, 16.8 s	9.2
Fe(abt) <sub>2</sub>	6,295	3.95	307.6	...	21.5 sh, 17.4 m, ~10.0 vs	7.6
Mn(abt) <sub>2</sub>	13,191	5.55	289.2	10	22.4 m, 16.6 m	0.3
Cr(abt) <sub>2</sub>	8,518	4.71	322.5	1	16.9 s	5.6
VO(abt) <sub>2</sub>	1,304	1.77	296.1	4	22.3 m, 19.0 w, 16.4 w	6.3

<sup>a</sup> Assuming the Curie-Weiss relation to be  $\chi_A = \text{constant}/(T + \theta)$ . <sup>b</sup> Diffuse reflectance spectra except for some solution spectra bands, for Co(abt)<sub>2</sub>, which have extinction coefficients in parentheses. <sup>c</sup> In  $10^{-3}$  M dimethylformamide solution at 25°.

distortions from octahedral symmetry remove the degeneracy of their <sup>4</sup>T<sub>1g</sub> ground terms, octahedral cobalt(II) complexes generally show a considerable variation of moment with temperature, but their reciprocal susceptibility *vs.* temperature plots are usually linear down to liquid nitrogen temperatures.<sup>10</sup> Tetrahedral cobalt(II) complexes usually show no variation of magnetic moment with temperature ( $\theta \sim 0^\circ$ ).<sup>10b</sup>

(10) (a) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962; (b) B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 37 (1964).

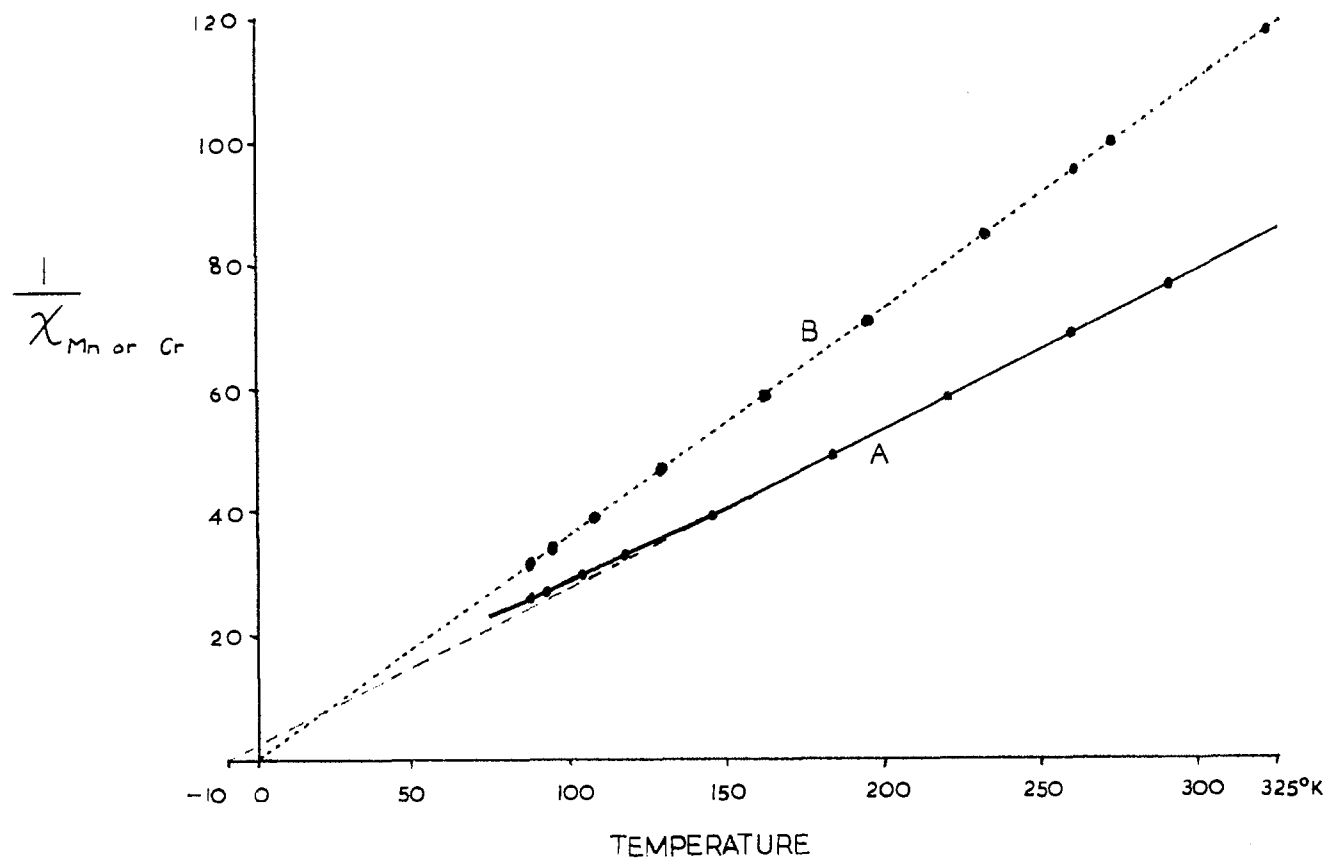


Figure 3.—Temperature dependence of the reciprocal magnetic susceptibility of (A)  $\text{Mn}(\text{abt})_2$  and (B)  $\text{Cr}(\text{abt})_2$ .

The magnetic behavior of  $\text{Co}(\text{abt})_2$  is that of an octahedral compound in which antiferromagnetic interactions enhance the normal variation of magnetic moment with temperature. To produce a six-coordinate structure sulfur bridging is necessary, and this is compatible with the poor solubility of the compound. The bridged structure would permit antiferromagnetic interaction *via* superexchange or direct coupling between metal atoms.

The reflectance spectrum of  $\text{Co}(\text{abt})_2$  has bands at 13,700 and 20,400  $\text{cm}^{-1}$  which can be assigned<sup>11</sup> to the transitions  ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}$  and  ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P})$ . It is very similar to that of the brown high-spin compound diiodobis(2,5-dithiohexane)cobalt(II) (bands at 20,400, 13,500, and also 7500  $\text{cm}^{-1}$ ), which is isomorphous with the corresponding octahedral nickel(II) compound.<sup>12</sup>

In DMF the presence of an absorption band at 16,600  $\text{cm}^{-1}$  ( $\epsilon$  293) suggests that a tetrahedral species is present. Low solubility prevented molecular weight or magnetic susceptibility measurements.

The compound  $\text{Fe}(\text{abt})_2$  has a  $\mu_e$  of 3.95 BM at 308°K. This low moment is due to magnetic exchange since the compound is antiferromagnetic, with a well-defined Néel point at 138°K (Figure 2). This appears to be the first iron(II) complex for which such behavior has been reported. It is possible to replicate reasonably the variation of atomic susceptibility  $\chi_A$  with temperature  $T$  by substituting  $J = 22.2 \text{ cm}^{-1}$ ,  $g = 2.07$ , and

$N(\alpha) = 0$  in eq 1 (Figure 2, solid line).  $J$  is the exchange coupling constant,  $g$  is the spectroscopic splitting factor,  $N(\alpha)$  is the temperature-independent contribution to the susceptibility,  $K = Ng^2\beta^2/3k =$

$$\chi_A = 3K/T \left[ \frac{30 + 14x^8 + 5x^{14} + x^{18}}{9 + 7x^8 + 5x^{14} + 3x^{18} + x^{20}} \right] + N(\alpha) \quad (1)$$

0.1251 $g^2$ , and  $x = e^{J/kT}$ . The other symbols have their usual significance. Equation 1 was derived on the assumption of exchange interactions between high-spin iron(II) atoms ( $S = 2$ ) in a binuclear system.<sup>13</sup> However, more highly polymerized systems would not differ markedly in magnetic behavior.<sup>14</sup>

The reflectance spectrum of  $\text{Fe}(\text{abt})_2$  is similar to that of other six-coordinate iron(II) complexes, containing a broad band near 10,000  $\text{cm}^{-1}$  which may be assigned to the  ${}^5\text{T}_{2g} \rightarrow {}^5\text{E}_g$  transition.<sup>10a, 15</sup> The magnetic and spectral properties and the poor solubility are compatible with a sulfur-bridged six-coordinate structure.

Slight antiferromagnetism is also found for cream  $\text{Mn}(\text{abt})_2$ . The Curie-Weiss constant for this compound is 10° and the reciprocal susceptibility *vs.* temperature plot departs from linearity at low temperatures (Figure 3). As before this is taken as

(13) K. Kambe, *J. Phys. Soc. Japan*, **5**, 48 (1950).

(14) A. Earnshaw, B. N. Figgis, and J. Lewis, *J. Chem. Soc.*, **A**, 1656 (1966).

(15) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press Ltd., London, 1962.

(11) J. Ferguson, *J. Chem. Phys.*, **32**, 533 (1960).

(12) R. L. Carlin and E. Weissberger, *Inorg. Chem.*, **3**, 611 (1964).

indicating a sulfur-bridged structure. Values of  $J = 1.6 \text{ cm}^{-1}$ ,  $g = 1.92$ , and  $N(\alpha) = 0$  in eq 2 gave a susceptibility *vs.* temperature plot which is close to the experimental curve. Equation 2 is the analog of eq 1

$$\chi_A = 3K/T \left[ \frac{55 + 30x^{10} + 4x^{18} + 5x^{24} + x^{28}}{11 + 9x^{10} + 7x^{18} + 5x^{24} + 3x^{28} + x^{30}} \right] + N(\alpha) \quad (2)$$

for high-spin manganese(II) with  $S = 5/2$ . The reflectance spectrum supports a six-coordinate structure, with bands attributable<sup>10a</sup> to the  ${}^6A_{1g} \rightarrow {}^4T_{1g}$  and  ${}^6A_{1g} \rightarrow {}^4T_{2g}$  transitions at 16,600 and 22,400  $\text{cm}^{-1}$ , respectively. Tetrahedral manganese(II) complexes are usually yellow-green, with absorptions more intense than those of octahedral complexes.<sup>16</sup> They do not usually absorb at as low an energy as the first  $\text{Mn}(\text{abt})_2$  band, which is in a common region for six-coordinate manganese(II).

Light blue  $\text{Cr}(\text{abt})_2$  could not be obtained completely pure and the analytical data suggest contamination with a little surplus ligand and possibly water. The high-spin complex has a broad band in its reflectance spectrum at 16,900  $\text{cm}^{-1}$ , typical of six-coordinate chromium(II) and assigned to the  ${}^5E_g \rightarrow {}^5T_{2g}$  transition.<sup>10a</sup>

**$\text{Cu}(\text{abt})$  and  $\text{VO}(\text{abt})_2$ .**—White, diamagnetic  $\text{Cu}(\text{abt})$  was obtained by direct reaction with ammoniacal cuprous chloride. A chain structure based on two-coordinate copper(I) with bridging ligand molecules is possible, but sulfur bridging could produce three- or four-coordinate copper.

Lime green  $\text{VO}(\text{abt})_2$  is a typical vanadyl(IV) complex. The V–O stretching absorption (997 and 989  $\text{cm}^{-1}$ , strong) is in the normal range for such complexes. The three bands in the reflectance spectrum may be assigned<sup>17</sup> in order of increasing energy to the  ${}^2B_2 \rightarrow {}^2E(I)$ ,  ${}^2B_2 \rightarrow {}^2B_1$ , and  ${}^2B_2 \rightarrow {}^2A_1$  transitions.  $\text{VO}(\text{abt})_2$  presumably has the usual square-pyramidal structure with apical oxygen.

#### Oxidation of *o*-Aminobenzenethiol Complexes.—

As already stated the air-sensitive nature of most *o*-aminobenzenethiol complexes has caused considerable confusion. Yellow  $\text{Ni}(\text{abt})_2$  turns green in air, rapidly if wet. This probably accounts for the green color recently reported<sup>7</sup> for it. The coloration is presumably due to the presence of traces of deep blue  $\text{Ni}(\text{NHC}_6\text{H}_4\text{S})_2$  which may be prepared in a pure state from the aerial oxidation of alkaline  $\text{Ni}(\text{abt})_2$ .<sup>2,4</sup> An oxygen-bridged formulation I was originally reported for this compound.<sup>5</sup> The absence of oxygen (Table I) and a mass spectrometric<sup>2</sup> molecular weight confirm structure II. The N–H stretching frequency data are also informative. All of the other complexes reported here have composite infrared absorption arising from the  $\text{NH}_2$  stretching modes (Figure 4 and Experimental Section). However,  $\text{Ni}(\text{NHC}_6\text{H}_4\text{S})_2$  has a single sharp band at 3300  $\text{cm}^{-1}$  arising from the NH stretching mode. The

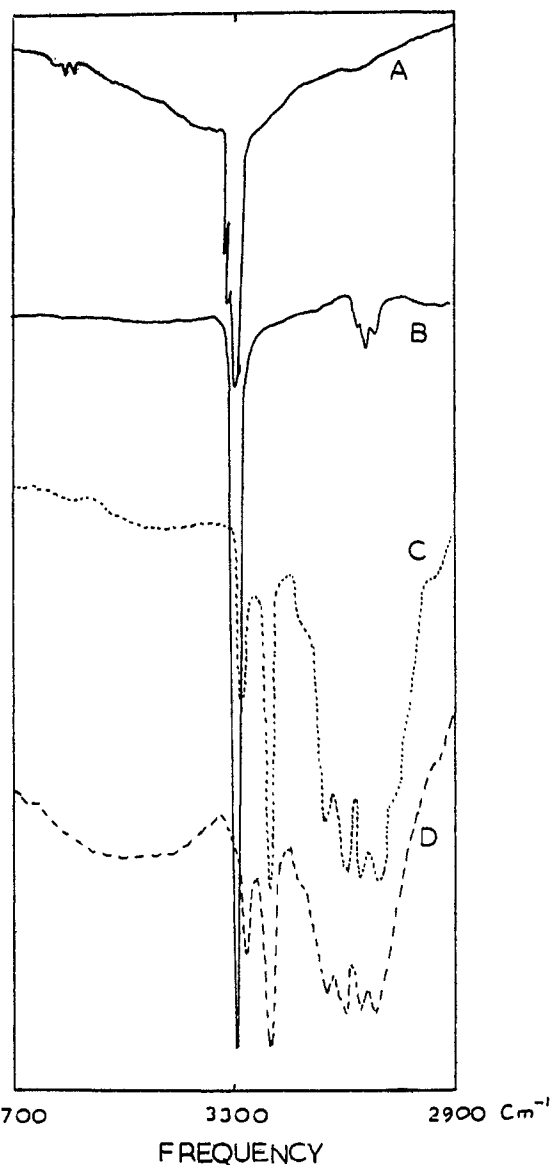


Figure 4.—Infrared spectra of (A)  $\text{Ni}(\text{NHC}_6\text{H}_4\text{NH})_2$ , (B)  $\text{Ni}(\text{NHC}_6\text{H}_4\text{S})_2$ , (C)  $\text{Co}(\text{abt})_2$ , and (D) " $\text{Co}(\text{abt})_2\text{OH}$ ."

related complex  $\text{Ni}(\text{NHC}_6\text{H}_4\text{NH})_2$  has a similar NH absorption consisting of a narrow triplet near 3300  $\text{cm}^{-1}$  (Figure 4). This triplet was not resolved by the instrument used in our earlier reported measurement on this compound.<sup>4</sup>  $\text{Ni}(\text{NHC}_6\text{H}_4\text{S})_2$  is diamagnetic and nonelectrolytic in DMF (Table III).

In the air orange-brown  $\text{Co}(\text{abt})_2$  turns dark brown when dry but forms a deep blue substance in boiling acetone. When first reported, the deep blue substance was assumed to be  $\text{Co}(\text{abt})_2$  on the basis of C, H, and N analyses, and the brown substance now known to be  $\text{Co}(\text{abt})_2$  was not examined.<sup>6</sup> A later report<sup>7</sup> that deep blue  $\text{Co}(\text{abt})_2$  results immediately from direct reaction between ligand and cobalt acetate in aqueous ethanol ignores the preliminary formation of orange-brown  $\text{Co}(\text{abt})_2$ , and, in this report,<sup>7</sup> the theoretical analysis figures for  $\text{Co}(\text{abt})_2$  are in error. A structure analogous to that of  $\text{Ni}(\text{NHC}_6\text{H}_4\text{S})_2$  for the oxidation product of  $\text{Co}(\text{abt})_2$  is unlikely since analytical data, including oxygen analyses, indicate formulation as " $\text{Co}(\text{abt})_2\text{OH}$ ,"

(16) D. M. L. Goodgame and F. A. Cotton, *J. Chem. Soc.*, 3735 (1961); F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1966.

(17) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, 1, 111 (1962).

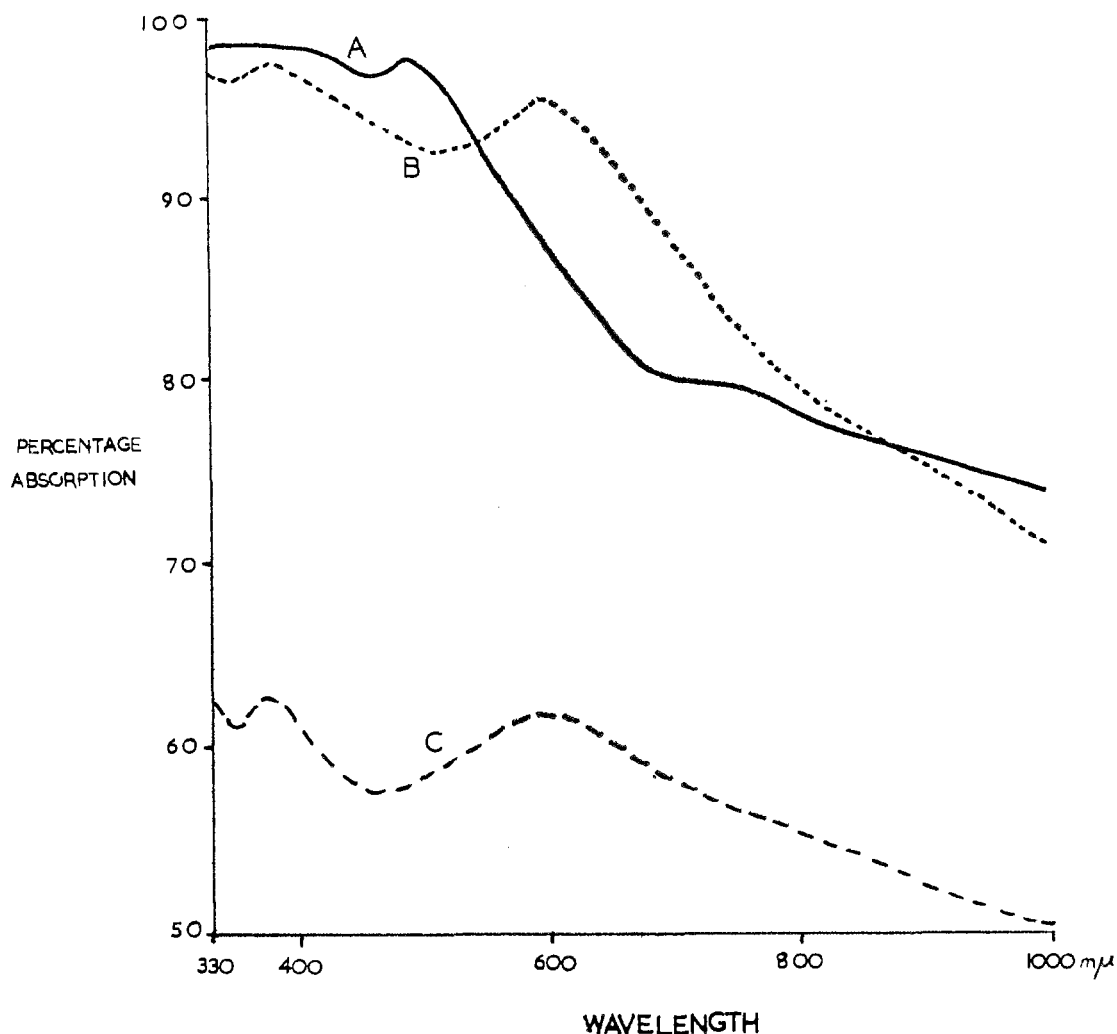


Figure 5.—Diffuse reflectance spectra of (A)  $\text{Co}(\text{abt})_2$ , (B)  $\text{Co}(\text{abt})_3$ , and (C) “ $\text{Co}(\text{abt})_2\text{OH}$ ” (diluted with magnesium carbonate).

TABLE IV  
SOME COBALT OXIDE AND HYDROXIDE COMPOUNDS

Compd	Ref to method of prepn	Magnetic moment, <sup>a</sup> $\mu_e$ , BM
$\text{CoO}_2$	<i>b</i>	0.8 <sup>b</sup>
$\text{CoO}_2$	<i>c</i>	0.7 <sup>c</sup>
$\text{Co}_2\text{O}_3$	<i>d</i>	2.3 <sup>d</sup>
$\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$	<i>e</i>	4.47 <sup>e</sup>
$\text{Co}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$	<i>f</i> (from $\text{Co}(\text{III})$ complex)	1.2 <sup>f</sup>
	<i>f</i> (from $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ )	0.9 <sup>f</sup>

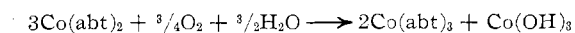
<sup>a</sup> The references below are to the determinations of  $\mu_e$ .

<sup>b</sup> V. A. Shcherbinin and G. A. Bagdanov, *Russ. J. Inorg. Chem.*, **4**, 112, (1959). <sup>c</sup> O. R. Howell, *Proc. Roy. Soc. (London)*, **A104**, 134 (1923). <sup>d</sup> E. H. Williams, *Phys. Rev.*, **28**, 167 (1926). <sup>e</sup> See ref 20. <sup>f</sup> G. F. Hüttig and R. Kassler, *Z. Anorg. Allgem. Chem.*, **184**, 279 (1929). <sup>g</sup> Present work.

and the substance has composite  $\text{NH}_2$  infrared stretching bands and a broad absorption in the OH stretching region (Figure 4). The substance has  $\mu_e = 2.6$  BM at 293°K. A similar value has been earlier reported<sup>6</sup> and has led to the blue oxidation product being accepted<sup>18</sup> as a typical low-spin, planar cobalt(II) complex.

(18) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 338 (1959); D. H. Busch, ACS Monograph 149, R. S. Young, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, Chapter 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.

Paramagnetism is not usual for oxidation products of cobalt(II) complexes. However, this substance shows striking resemblances to the dark green but diamagnetic complex  $\text{Co}(\text{abt})_3$  which is discussed below. First, the reflectance spectra are very similar, apart from differing base line slopes (Figure 5). Second, the infrared spectra are almost identical apart from the OH absorption in dark blue “ $\text{Co}(\text{abt})_2\text{OH}$ ” (Figure 4 and Experimental Section). Finally, the X-ray powder photographs are almost identical (Table II). It appears that, in the formation of the oxidation product, ligand transfer occurs to give a mixture of  $\text{Co}(\text{abt})_3$  and some finely divided, dark cobalt hydroxide species in the analytically appropriate proportions. A possible reaction is



The cobalt hydroxide species would presumably account for the OH infrared absorption and the paramagnetism of “ $\text{Co}(\text{abt})_2\text{OH}$ .” If, as seems likely,<sup>19</sup> it is amorphous to X-rays, it would add no extra lines to the powder photograph. Hydrrous  $\text{Co}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  fits the analytical data well, but all samples which we have prepared are low spin.  $\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$  has a magnetic

(19) A. Krause and W. Wojciechowska, *Roczniki Chem.*, **31**, 1137 (1957).

moment of the right magnitude<sup>20</sup> but does not suit the analytical data so well. Other oxides examined have low magnetic moments (Table IV). The magnetic properties of cobalt and other metallic oxides vary enormously with the method of preparation, physical state, and quantity of water present.<sup>21</sup> The method of preparation of the dark blue substance may be such that magnetically dilute, high-moment hydroxide species are obtained which cannot be reproduced in bulk preparations.

Dark blue "Co(abt)<sub>2</sub>OH" can be obtained with reasonably reproducible analyses and magnetic and spectral properties by boiling Co(abt)<sub>2</sub> in acetone in the air as described. However, aerial oxidation in other conditions, *e.g.*, in acetone or aqueous alkali at room temperature, gives dark blue paramagnetic materials with unreproducible properties. Such variable behavior is indicative of the formation of mixtures.

The reported preparation<sup>5</sup> of diamagnetic Co(abt)<sub>3</sub> by reaction between ligand and CoCl<sub>2</sub> in aqueous ammoniacal ethanol under nitrogen could not be repeated, and the compound was obtained by reaction in air. The complex is a nonelectrolyte in DMF and has a reflectance spectrum typical of six-coordinate cobalt(III). The two bands in order of increasing energy are assigned to the <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>1g</sub> and <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>2g</sub> transitions, respectively.<sup>10a</sup>

The reported preparation<sup>7</sup> of deep blue Cu(abt)<sub>2</sub> from

(20) J. T. Richardson and L. W. Vernon, *J. Phys. Chem.*, **62**, 1153 (1958).

(21) J. Amiel and J. Besson, "Nouveau Traite de Chimie Minerale," Vol. XVII, P. Pascal, Ed., Masson et Cie, Paris, 1963, p 317.

direct reaction between ligand and cupric salts in aqueous ethanol seems to be in error. On repeating the preparation, a white mixture of Cu(abt) and (NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>S)<sub>2</sub> was obtained. The cupric ion has oxidized *o*-aminobenzenethiol to the disulfide, yielding a mixture of empirical formula Cu(abt)<sub>2</sub>. Stabilization of copper(I) by sulfur ligands is well known.<sup>22</sup> The Cu(abt) produced, when present in the mixture or in the pure state, rapidly darkens in air. This probably accounts for the blue color reported for the reaction product. In this case the blue oxidation product has not been identified. Aerial oxidation of cuprous ion and ligand and subsequent oxidation of ligand by cupric ion are all possible so that complex oxidation products are likely with Cu(abt). The ferrous system is similarly complicated.

**Further Observations.**—The original reports<sup>6,7,18</sup> of Co(abt)<sub>2</sub> as low-spin suggested that *o*-aminobenzenethiol should be classified as a high-field ligand. However, in all of the complexes where different spin multiplicities are possible high-spin complexes are formed, except with nickel(II) and cobalt(III). Visible spectra confirm the weak-field nature of the ligand, which on the basis of the spectrum of Co(abt)<sub>3</sub> is comparable to water in ligand field strength.

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(22) S. E. Livingstone, *Quart. Rev. (London)*, **19**, 386 (1965).

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## Deprotonation of *o*-Aminophenol and *o*-Aminothiophenol Complexes of Nickel(II) and Palladium(II)

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In the absence of air, *o*-aminophenol and *o*-aminothiophenol complexes of nickel(II) and palladium(II) are deprotonated by potassium amide in liquid ammonia and form potassium salts of the corresponding anions. These salts react with water to regenerate the parent complexes and with methyl iodide to form S-, O-, and N-methylated derivatives.

*o*-Aminophenol and *o*-aminothiophenol complexes of the type M(H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>X)<sub>2</sub>, where M = Ni, Pd and X = O, S, are well known;<sup>1-5</sup> recently a "metal-stabilized radical-ligand complex" of the composition Ni(H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>S)<sub>2</sub> has been prepared by atmospheric oxidation of bis(*o*-aminothiophenolato)nickel(II) in alkaline solu-

tion.<sup>6</sup> Polarographic reduction of this salt in dimethyl sulfoxide and dichloromethane solutions gave evidence for the existence of the bis(*o*-amidothiophenolato)-nickelate(II) complex, [Ni(HNC<sub>6</sub>H<sub>4</sub>S)<sub>2</sub>]<sup>2-</sup>, but solid derivatives of this ion were not isolated.<sup>7</sup>

We have found, however, that careful treatment of M(H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>X)<sub>2</sub> complexes with solutions of potassium

(1) W. Hieber and A. Schnackig, *Z. Anorg. Allgem. Chem.*, **226**, 209 (1936).

(2) W. Hieber and R. Brück, *Naturwissenschaften*, **36**, 312 (1949).

(3) W. Hieber and R. Brück, *Z. Anorg. Allgem. Chem.*, **269**, 13 (1952).

(4) S. E. Livingstone, *J. Chem. Soc.*, 437, 1042 (1956).

(5) E. J. Olszewski and M. J. Albinak, *J. Inorg. Nucl. Chem.*, **27**, 1431 (1965).

(6) E. I. Stiefel, J. H. Waters, E. Billig, and H. B. Gray, *J. Am. Chem. Soc.*, **87**, 3018 (1965).

(7) R. H. Holm, A. L. Balch, A. Davidson, A. H. Maki, and T. E. Berry, *ibid.*, **89**, 2866 (1967); A. L. Balch, F. Röhrschied, and R. H. Holm, *ibid.*, **87**, 2301 (1965).