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Aromatic Diamine Complexes. II. Tetragonal Distortion in some Cobalt(II) Complexes

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Received April 14, 1970

The synthesis of six coordinate cobalt(II) complexes containing two and three molecules of the aromatic diamines o-phenylenediamine*, 1,8-diaminonaphthalene, and 2,2′ diaminobiphenyl is described. The complexes have been characterized by magnetic and vibrational and electronic spectral measurements. The complexes containing two molecules of diamine are assigned* trans *structures and their visible and near infrared spectra explained on the basis of tetragonal distortion, with local molecular symmetry D_{4h} or D_{2h} about the cobalt(II) ion.*

Introduction

In Part I of this series[2] we reported the preparation and characterization of nickel(II) complexes containing two and three molecules of the aromatic diamines, *o*-phenylenediamine (opda), 1,8-diaminonaphthalene (dan) and 2,2′-diaminobiphenyl (dabp). The tetragonal structures assigned to the complexes containing two molecules of diamine per nickel(II) ion were deduced from their infrared and visible spectra. In view of the generality of this structure for nickel(II) complexes with these aromatic diamines and the lack of information on cobalt(II) complexes of similar structure, the investigation here reported was carried out.

In 1929, Hieber *et al.*[3] prepared cobalt(II) complexes with one, two, four or six molecules of *o*-phenylenediamine and since that time the isolation of several cobalt(II) complexes with this ligand have been reported.[4-8] For the other two ligands, some complexes with two molecules of diamine per cobalt(II) ion have been prepared but little investigated.[9-11]

In this paper we report the synthesis and characterization of cobalt(II) complexes containing two and three molecules of the three aromatic diamines.

Experimental Section

o-Phenylenediamine, 1,8-diaminonaphthalene, and 2,2′-diaminobiphenyl were obtained and purified as previously described.[2] Cobalt perchlorate was prepared from cobalt carbonate and perchloric acid and recrystallized from ethanol. Cobalt thiocyanate was prepared in situ by the reaction of cobalt nitrate in ethanol with potassium thiocyanate. The precipitated potassium nitrate was removed by filtration and the ethanolic filtrate used for the preparation of the complexes.

The complexes containing 2,2′-diaminobiphenyl were prepared by the addition of a warm ethanolic solution of the cobalt salt (0.001 mole) to a warm stirred solution of the diamine (0.003 mole). The precipitated pink colored complexes were removed by filtration, washed with ethanol and dried under vacuum. They are air stable. The complexes containing *o*-phenylenediamine and 1,8 diaminonaphthalene were prepared under nitrogen using a chloroform-methanol mixture (70-30 V/V) as solvent, which had been deoxygenated by passing oxygen free nitrogen through for several hours before use. The quantities of cobalt salt and diamine used were as above. The precipitated complexes were removed by filtration, washed with solvent and dried under vacuum. They are obtained as pink or brick red powders, which are stable under nitrogen, but decomposed by air or moisture.

Infrared spectra, magnetic susceptibility measurements and reflectance spectra on solid samples were obtained as previously described.[2]

Results and Discussion

The complexes obtained by the reaction of *o*-phenylenediamine, 1,8-diaminonaphthalene and 2,2′-diaminobiphenyl with various cobalt(II) salts are listed in Table I, together with their analytical data. The complexes with *o*-phenylenediamine and 1,8-diaminonaphthalene are readily decomposed by air and moisture and consequently were prepared and handled

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Table I. Analytical and Magnetic Data for the Complexes

Compound	Calculated % C	H	N	Found % C	H	N	$\chi_m^{corr} \times 10^6$	T°K	μ_{eff} BM
Co(opda)$_2$Br$_2$	33.10	3.67	12.87	33.13	3.67	12.71	10660	292	5.00
Co(opda)$_2$(NO$_3$)$_2$	36.09	4.61	21.05	36.12	4.33	20.84	10800	293	5.05
Co(opda)$_2$(NCS)$_2$	42.96	4.09	21.48	43.03	4.60	20.82	10390	294	4.97
Co(opda)$_3$(ClO$_4$)$_2$	37.17	4.13	14.43	37.18	4.20	14.48	10280	293	4.93
Co(dan)$_2$Cl$_2$	54.04	4.48	12.55	53.92	4.57	12.44	10000	293	4.87
Co(dan)$_2$Br$_2$	44.85	3.73	10.48	44.62	3.98	10.30	10150	293	4,91
Co(dan)$_2$I$_2$	38.15	3.17	8.90	38.36	3.25	8.95	10360	293	4.95
Co(dan)$_2$(NO$_3$)$_2$	48.09	4.01	16.83	48.03	4.12	16.69	10510	292	4.97
Co(dan)$_2$(NCS)$_2$	53.77	4.07	17.10	53.89	4.52	16.02	11120	293	5.10
Co(dan)$_3$(ClO$_4$)$_2$	49.18	4.10	11.49	48.83	4.91	11.30	10750	293	5.04
Co(dabp)$_2$Cl$_2$	57.90	4.80	11.26	58.08	5.15	10.48	10340	292	4.94
Co(dabp)$_2$Br$_2$	49.06	4.08	9.54	48.83	4.50	9.48	10890	292	5.05
Co(dabp)$_2$I$_2$	42.29	3.52	8.22	42.72	3.55	8.40	10460	292	4.94
Co(dabp)$_2$(NO$_3$)$_2$	52.25	4.36	15.24	53.48	4.67	14.99	10730	291	5.00
Co(dabp)$_2$(NCS)$_2$	57.45	4.41	15.45	57.05	4.94	14.48	10800	291	5.02
Co(dabp)$_3$(ClO$_4$)$_2$	53.33	4.44	10.90	51.82	4.44	10.50	10305	291	4.92

Table II. Characteristic Infrared Absorption Bands, 4000-40 cm^{-1}

Compound	ν(N—H)	δ(NH$_2$)	ν(C—N)	Anion X	ν(Co—X)	δ(Co—X)	ν(Co—N$_{lig}$)
opda	3380, 3360 3280, 3180	1620	1270	—	—	—	—
Co(opda)$_2$Br$_2$	3320, 3250 3210, 3170	1610	1250	—	120	100	284
Co(opda)$_2$(NO$_3$)$_2$	3340, 3290 3260, 3180	1605	1255	1410, 1310 1035	144	—	284
Co(opda)$_2$(NCS)$_2$	3300, 3280 3230, 3160	1600	1250	2100, 785 465	174	—	280
Co(opda)$_3$(ClO$_4$)$_2$	3340, 3280 3240, 3180	1610	1250	1180-1000 (br)	—	—	280 (br)
dan	3410, 3380 3330, 3300	1620	1260	—	—	—	—
Co(dan)$_2$Cl$_2$	3280, 3260 3180, 3130	1610	1235	—	132	84	300
Co(dan)$_2$Br$_2$	3280, 3250 3180, 3140	1610	1240	—	108	60	300
Co(dan)$_2$I$_2$	3310, 3280 3220, 3160	1600	1225	—	76	52	296
Co(dan)$_2$(NO$_3$)$_2$	3300, 3260 3230, 3160	1605	1230	1420, 1315 1030	132	—	292
Co(dan)$_2$(NCS)$_2$	3300, 3270 3230, 3160	1610	1235	2090, 790 462	146	—	276
Co(dan)$_3$(ClO$_4$)$_2$	3320, 3300 3270, 3150	1610	1230	1180-1040 (br)	—	—	286 (br)
dabp	3400, 3380 3270, 3170	1630	1250	—	—	—	—
Co(dabp)$_2$Cl$_2$	3300, 3280 3220, 3180	1600	1230	—	226	106	296
Co(dabp)$_2$Br$_2$	3280, 3200 3160	1610	1230	—	162	92	294
Co(dabp)$_2$I$_2$	3270, 3200 3150, 3120	1600	1235	—	124	84	294
Co(dabp)$_2$(NO$_3$)$_2$	3320, 3300 3240, 3150	1620	1225	1410, 1305 1030	220	—	304 (sh)
Co(dabp)$_2$(NCS)$_2$	3340, 3320 3240, 3140	1605	1220	2100, 780 460	204	—	264
Co(dabp)$_3$(ClO$_4$)$_2$	3340, 3320 3290, 3240 3140	1600	1230	1170-1010 (br)	—	—	294, 268

br, broad; sh, shoulder on ligand absorption.

under nitrogen. However, with the 2,2′-diaminobiphenyl complexes no decomposition was observed in air and consequently no precautions to exclude air or moisture, during preparation or handling, were taken. The reaction of *o*-phenylenediamine with cobalt chloride results in the isolation of Co(opda)Cl$_2$ and Co(opda)$_4$Cl$_2$ depending on the ratio of ligand to cobalt used. The former compound, and the corresponding bromide, have been assigned tetrahedral structures,[6] and the latter compound probably contains both unidentate and bidentate diamine similar to the nickel(II)[12] and iron(II)[13] complexes with four ligands. These compounds will not be discussed further here. The product from the reaction of cobalt iodide with *o*-phenylenediamine contains two molecules of diamine per cobalt(II), but it was very easily oxidized even when dry. Data obtained for this compound were not reproducible and are not reported here.

Characteristic infrared absorption bands for both free and coordinated ligands, and anions where applicable, are listed in Table II. It can readily be seen that for the three ligands, coordination to cobalt(II) results in lowering of bands assigned to the ν(N–H), δ(NH_2), and ν(C–N) frequencies in all cases. Similar shifts were observed for the nickel(II) complexes containing these ligands[2] and it is concluded that in the cobalt complexes reported here, all three diamines are behaving as bidentate ligands. For the nitrate ions, the infrared evidence suggests the presence of unidentate coordination[14] and for the thiocyanates, coordination through the nitrogen atom of the group.[15] The perchlorates all have strong, broad absorptions indicative of uncoordinated perchlorate ions.[16]

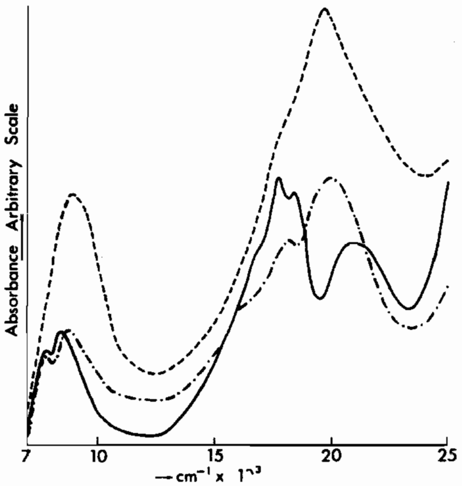

Figure 1. Spectra of 2,2′ diaminobiphenyl complexes. ——— $Co(dabp)_3(ClO_4)_2$; —.—.— $Co(dabp)_2Cl_2$; ——— $Co(dabp)_2I_2$.

The room temperature magnetic properties of the complexes are reported in Table I. All the complexes have magnetic moments in the region of 4.9-5.1 Bohr magnetons, indicating an octahedral or distorted octahedral environment about the cobalt(II) ion.[17] Thus for the 3:1 complexes, the cobalt(II) ion is surrounded by six donor nitrogen atoms, whereas for the 2:1 complexes the metal ion has four nitrogen donors and two anions as the coordination environment. The absorption bands that were identified as arising from cobalt-ligand and cobalt-anion vibrations are shown in Table II. For the 3:1 complexes, strong, broad bands in the region of 300 cm^{-1} are the main features of the infrared spectra between 400 and 40 cm^{-1}. These bands are assigned to cobalt-ligand stretching vibrations (ν(Co–N_{lig}) in Table II). The 2:1 complexes have spectra in the far infrared region that are very similar to those of the corresponding nickel complexes previously described.[18] One strong band, which is anion dependent, is assigned to the cobalt-anion stretching vibration (ν(Co–X)). This indicates that the 2:1 complexes have the *trans* configuration, with the two diamine ligands in a plane and the anions coordinated in axial positions above and below this plane. The spectra also have a strong band in the region of 300 cm^{-1} corresponding to ν(Co–N_{lig}). The positions of ν(Co–X) for the diaminonaphthalene complexes are considerably lower than those found for complexes with the other two ligands and for some cobalt(II) complexes of D_{4h} symmetry[19,20] and suggest that the complexes exhibit considerable tetragonal distortion. It was found previously[2] that the 2:1 nickel(II) complexes containing diaminonaphthalene were more tetragonally distorted than the complexes with *o*-phenylenediamine and diaminobiphenyl.

The electronic absorption spectra provide further information concerning the structure of the complexes and the localized environment of the cobalt(II) ion. The free ion ground term is ^4F with the excited state ^4P located at higher energy. In the presence of an octahedral crystal field, (O_h symmetry), these levels split into $^4T_{1g}(F)$, $^4T_{2g}(F)$, $^4A_{2g}(F)$ and $^4T_{1g}(P)$ in order of increasing energy. Thus three transitions from the ground state $^4T_{1g}(F)$ to higher states are expected, and should give rise to absorptions in the near infrared and visible regions of the spectrum. The reflectance spectra of the 3:1 complexes are shown in Table III. In these complexes, the cobalt(II) ion is surrounded by six donor nitrogen atoms and the following assignments may be made:

$$\nu_1,\ {}^4T_{1g}\rightarrow{}^4T_{2g};\ \ \nu_2\ \ {}^4T_{1g}\rightarrow{}^4A_{2g};\ \ \nu_3\ \ {}^4T_{1g}\rightarrow{}^4T_{1g}\ (P)$$

The position of ν_2 is not quoted with great accuracy as it occurs as a shoulder on the low energy side of the absorption band assigned to ν_3. This is usually the situation encountered for ν_2 as it corresponds to a two electron transition and possesses only a small intensity.[21] The difference in energy between the ν_1 and ν_2 transitions should be equal to 10 Dq and provide a value for the ligand field strength of each diamine. The values obtained for 10 Dq range between 9000 and 10000 cm^{-1} for the three diamines and are similar to those derived from the spectra of 3:1 complexes of these ligands with nickel(II).[2] However, the difficulty of locating the position of the ν_2 absorption band means that accurate values of 10 Dq cannot be obtained.

The complexes containing two molecules of diamine per cobalt(II) ion give rise to spectra in which the ν_1 and ν_3 bands are either much broader than those of the 3:1 complexes or consist ofseveral com-

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(17) B. N. Figgis and J. Lewis, *Prog. Inorg. Chem.*, Vol. 6, p. 186, Interscience, New York (1964).

(18) See Reference 2. The position of ν(M—X) for the complex $Ni(dabp)_2Br_2$ should be 174 cm^{-1} (Table V of the paper).

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(20) R. H. Nuttall and G. A. Melson, *J. Inorg. Nucl. Chem., 31*, 2979 (1969).

(21) C. J. Ballhausen, « Introduction to Ligand Field Theory », McGraw-Hill, New York, 1962, p. 256.

Table III. Reflectance Spectra Between 7000 and 25000 cm^{-1}

Compound	ν_1	ν_2	ν_3
$Co(opda)_3(ClO_4)_2$	9800	18800 sh	20200
$Co(dan)_3(ClO_4)_2$	8500	18200 sh	20700
$Co(dabp)_3(ClO_4)_2$	9000	18200 sh	19700
$Co(opda)_2Br_2$	9500	18600 sh	20600 hr
$Co(opda)_2(NO_3)_2$	9500	18400 sh	20500 br
$Co(opda)_2(NCS)_2$	10500 sh, 9400 sh	17800 sh	20500 br
$Co(dan)_2Cl_2$	8000 sh, 9500 sh	16500 sh	17700, ~19700
$Co(dan)_2Br_2$	8000 sh, 9500 sh	~16200 sh	17500, 20500
$Co(dan)_2I_2$	8000 sh, 9500 sh	16500 sh	18000-20800 br *
$Co(dan)_2(NO_3)_2$	9000 br, sh	16500 sh	19300, 21000 br
$Co(dan)_2(NCS)_2$	10900 sh, 9500 sh	~16800 sh	21800, 20700
$Co(dabp)_2Cl_2$	7800, 8800	16200 sh	18200, 20100
$Co(dabp)_2Br_2$	7800, 8600	17250 sh	18200, 19000, 20400
$Co(dabp)_2I_2$	7800, 8500	16700 sh	17700, 18400, 20800
$Co(dabp)_2(NO_3)_2$	7800, 9400	16800 sh	19600, 20600
$Co(dabp)_2(NCS)_2$	10650, 8900	17800 sh	21800, 20300

* Spectrum not well resolved. br, broad; sh, shoulder.

ponents. The infrared spectra of the 2:1 complexes suggest that the local symmetry about the cobalt(II) ion is D_{4h} (or D_{2h} if the bidentate nature of the ligands is considered). The visible and near infrared spectra of these complexes can be rationalized by considering the effect of the reduction in symmetry from O_h to D_{4h} on the exicted states of the cobalt(II) ion. The first excited state ($^4T_{2g}$ (F) in O_h symmetry) will split into two components, ^4E_g and $^4B_{2g}$, the $^4A_{2g}$ state will become $^4B_{1g}$ and the $^4T_{1g}$ (P) state will also split into two components, ^4E_g and $^4A_{2g}$ in D_{4h} symmetry. Thus the ν_1 and ν_3 absorption bands observed in O_h symmetry should each consist of two components in D_{4h} symmetry, while the ν_2 band should still correspond to a single transition. If the tetragonal distortion is small, broadening of the ν_1 and ν_3 absorption bands will be observed, but as the distortion is increased, the ν_1 and ν_3 bands should be resolved into their components.

At this point the ordering of the energy levels in D_{4h} symmetry should be considered. The relative axial and inplane ligand field strengths should determine which of the two states, ^4E_g or $^4B_{2g}$ (from $^4T_{2g}$ in O_h symmetry) is the lower in energy. If the axial ligand field strength (Dq^z) is less than the inplane ligand field (Dq^{xy}), the tetragonal distortion will be « positive », *i.e.*, the octahedron will be elongated along the z axis and the ^4E_g state will be lower in energy than the $^4B_{2g}$ state. However, if Dq^z is greater than Dq^{xy}, the reverse situation will occur and the $^4B_{2g}$ state will be lower than the ^4E_g state. A similar argument may be applied to the ^4E_g and $^4A_{2g}$ states arising from $^4T_{1g}$ (P) in O_h symmetry.

Thus for $Dq^z < Dq^{xy}$, the order of excited states for the cobalt(II) ion in D_{4h} symmetry will be:

$$^4E_g < {}^4B_{2g} < {}^4B_{1g} < {}^4E_g < {}^4A_{2g}$$

For $Dq^z > Dq^{xy}$, the order will be:

$$^4B_{2g} < {}^4E_g < {}^4B_{1g} < {}^4A_{2g} < {}^4E_g$$

The spectra of the complexes containing two molecules of diamine per cobalt(II) ion are shown in Table III. The complexes with 2,2′-diaminobiphenyl gave the best resolved spectra and these will be discussed first. For the chloro and nitrato complexes, the ν_1 and ν_3 bands (using the notation for O_h symmetry) each consist of two bands, suggesting a considerable tetragonal distortion is present. For these complexes, the axial ligand field strength, due to the coordinated anions, is assumed to be less than the inplane ligand field due to the diamines. (Calculations for the corresponding nickel(II) complexes[2] showed Dq^z to be less than Dq^{xy}). Consequently, the low energy component of the ν_1 band is assigned as a transition from the ground state to the ^4E_g state, the higher energy component being assigned as a transition to the $^4B_{2g}$ state. The ν_2 band remains as a shoulder with no structure on the low energy component of the ν_3 band (transition to ^4E_g) with the transition to $^4A_{2g}$ several hundred wavenumbers higher in energy. Further evidence to support the order of energy levels is found in the spectra of the bromo and iodo complexes, where Dq^z should be much less than Dq^{xy} and consequently a large tetragonal distortion should be present. For the ν_1 absorption band, two separate peaks are again observed, but for the ν_3 band, the low energy component is further resolved into two bands, the higher energy component remaining in approximately the same position as that found for the chloro and nitrato complexes. This splitting of the low energy component of ν_3 can be understood if we assume that the degeneracy of the ^4E_g state is removed. If we consider the molecular symmetry about the cobalt(II) ion to be D_{2h}, it is expected that the ^4E_g state in D_{4h} symmetry will become $^4B_{2g}$ and $^4B_{3g}$ in D_{2h} symmetry. Since it is the low energy component of the ν_3 band which is split, it must be that in D_{4h} symmetry when $Dq^z < Dq^{xy}$ the ^4E_g state lies below the $^4B_{2g}$ state in energy. Consequently in the bromo and iodo complexes, the ν_3 band is composed of transitions from the ground state to the excited states $^4B_{3g}$, $^4B_{2g}$ and $^4B_{1g}$. The presence of three components for the «ν_3» band has also been noted by Ferguson[22] in the spectrum of the polymeric form of $Copy_2Cl_2$, (py = pyridine). This complex also has D_{2h} symmetry. Ideally, splitting of the low energy compo-

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[22] J. Ferguson, *J. Chem. Phys.*, 32, 533 (1960).

nent of the ν_1 band should also occur, but this was not detected experimentally.

For the isothiocyanato complex, the ν_1 and ν_3 bands each consist of two components. However, in both cases, the position of one of the bands is similar to that of the « high energy » component observed for the other complexes, with another band located some 1500 cm^{-1} higher in energy. No band is present corresponding to the « low energy » component of the other complexes.

This can be rationalized if we consider that Dq^z is now greater than D^{xy}. (This conclusion was reached for the corresponding nickel(II) complex[2]). If this is the case, the ^4E_g state is at higher energy than $^4B_{2g}$ and ^4E_g is higher than $^4A_{2g}$ as explained earlier. Thus the band at 8900 cm^{-1} is assigned as a transition from the ground state to the $^4B_{2g}$ state and that at 10650 cm^{-1} as a transition to ^4E_g. Similarly, the 20300 cm^{-1} band is a transition to the $^4A_{2g}$ state and the 21800 cm^{-1} band a transition to ^4E_g.

For the diaminobiphenyl complexes, the separation between the highest and lowest energy components of the ν_3 absorption band is dependent on the nature of the axial groups. Thus the separation increases as:

$$NCS^- < NO_3^- < Cl^- < Br^- < I^-$$

which is just the reverse of the expected spectrochemical series for these anions. (The value for NCS^- is in the opposite direction to that for the other groups). Hence, the separation between the components is related to the degree of tetragonal distortion present in the complex.

Recently, Lever and Ogden[23] studied the spectra of some cobalt(II) haloacetate complexes with pyridine. Similar spectra to those described above were observed. The «ν_3» absorption band is composed of a peak and shoulder, with the shoulder moving from the low energy side of the peak to the high energy side as the axial ligand field becomes greater than the inplane ligand field. However, they assigned the peak as a transition to the ^4E_g state, with the shoulder corresponding to excitation to the $^4A_{2g}$ state.

The spectra of the *o*-phenylenediamine complexes show broadening of the ν_1 and ν_3 bands for the bromo and nitrato derivatives. The tetragonal distortion in these complexes must consequently be quite small, as separation into components is not observed. The isothiocyanato derivative, however, does show a « high energy » component of the ν_1 band similar to that found for the diaminobiphenyl complex, and again we may assume that Dq^z from the coordinated thiocyanate group is greater than Dq^{xy} from the aromatic diamines.

The diaminonaphthalene complexes, although giving rise to rather poorly defined spectra, do show splitting of both the ν_1 and ν_3 absorption bands into two components, and the reversal of positions for the isothiocyanato complex. The far infrared spectra of these complexes suggest that large tetragonal distortions are present, particularly in the halide derivatives, and it is relevant to note that the separations between the components of ν_1 and ν_3 are larger for these complexes than for the complexes with the other ligands, although the relative ordering is the same as discussed earlier.

(23) A. B. P. Lever and D. Ogden, *J. Chem. Soc.* (A), 2041 (1967).