Preparation and Magnetic and Spectral Studies of Some Cobalt(II) Complexes of Benzimidazole

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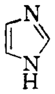
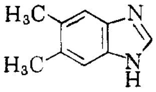
The following benzimidazole, HBZD, complexes of Co(II) have been prepared: Co(BZD)$_2$, [Co(HBZD)$_4$](ClO$_4$)$_2$, [Co(HBZD)$_2$X$_2$] in which X = Cl, Br, I or NO$_3$, [(C$_2$H$_5$)$_4$N][Co(HBZD)Br$_3$] and [CH$_3$(C$_6$H$_5$)$_3$As][Co(HBZD)I$_3$]. Detailed spectral and magnetic studies of these compounds show that the imidazole group, at least as it occurs in benzimidazole, lies very far toward the strong end of the spectrochemical series. It is, in fact, the strongest ligand (in this respect) which has so far been found coördinated to tetrahedral Co(II).

Introduction

The imidazole nucleus, I, and derivatives thereof are known to play extremely crucial parts in the structures and functioning of a number of biologically important molecules, generally by virtue of their being coördinated to metal ions. Thus dimethylbenzimidazole, II, supplies one of the five nitrogen atoms coördinated to Co(III) in vitamin B$_{12}$ and several of its derivatives, and there is strong evidence that in proteins containing heme as a prosthetic group, *e.g.*, hemoglobin, myoglobin, cytochrome c, imidazole nitrogen atoms, probably in histidine residues, III, of the proteins, are coördinated to the iron atoms.


I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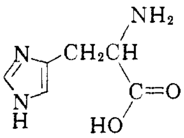
III

The interactions of several imidazole-containing ligands with metal ions are being studied in these Laboratories. This paper reports some studies of the complexes of Co(II) with benzimidazole.

The literature contains some previous reports of complexes containing (presumably coördinated) imidazole groups. Aside from a vast number of studies of stability constants of histidine complexes of various metal ions there are the studies of Hearon, *et al.*,[2] on histidine complexes of Co(II) and the work of Nortia[3] on some histamine complexes of Cu(II) and Ni(II), and several studies of imidazole and substituted imidazole complexes of various metals.[4-7] Reports of the actual isolation and characterization of complexes containing coördinated imidazole groups are relatively few. Some complexes have been isolated with metals other than cobalt.[8-12] Previous reports of Co(II) complexes include descriptions of the preparation of bis-benzimidazolatocobalt(II)[11-14] and its suggested use for quantitative separation of Co(II) and of the preparation of a series of complexes of general formula CoL$_2$X$_2$ in which L was one of several substituted benzimidazoles and X one of the anions Cl$^-$, Br$^-$, SCN$^-$, NO$_3^-$.[15] None of these compounds was studied spectroscopically or magnetically. Bis - benzimidazolato - Co(II) has been reported[12] to have a magnetic moment of 3.85 B.M., but since the calculated analyses for this and other compounds reported in this paper are erroneous, this result is of no value. Thus there is virtually nothing known heretofore of the magnetic and spectral properties, configurations and electronic structures of complexes containing coördinated imidazole groups.

Because the considerable body of information on the relationship of magnetic and spectral characteristics to molecular and electronic structures of Co(II) complexes makes the Co(II) ion a most useful probe for such investigations,[16] we explored the possibility of isolating Co(II) complexes of benzimidazole. On finding that a variety of tetrahedral complexes could be prepared, these complexes were subjected to detailed magnetic and spectral studies, yielding information on the strengths of the ligand fields produced by the ligand benzimidazole.

Experimental

Preparation of Compounds. Bis-(benzimidazolato)-Co(II).—11.8 g. (0.1 moles) of benzimidazole in 80 ml. of hot water was added to 15 g. (0.065 mole) of Co(NO$_3$)$_2$·6H$_2$O in 20 ml. of hot water. The mixture was heated to boiling, when most of the precipitate which had first formed redissolved. On cooling, a deep purple precipitate was formed. This was filtered, washed and dried *in vacuo*. Yield: 5.4 g. (37%), m.p. above 400°.

Anal. Calcd. for C$_{14}$H$_{10}$CoN$_4$: C, 57.35; H, 3.44; N, 19.11. Found: C, 57.63; H, 3.48; N, 19.23.

Dichlorobis-(benzimidazole)-Co(II).—4.72 g. (0.04 mole) of benzimidazole in 10 ml. of absolute ethanol was added to a solution of 4.76 g. (0.02 mole) of CoCl$_2$·6H$_2$O in 10 ml. of absolute ethanol. 20 ml. of benzene was added, and the solution evaporated on a steam-bath to small bulk. The solid formed was crushed, triturated with 20 ml. of absolute ethanol, then filtered, washed and dried *in vacuo*. Yield: 5.8 g. (71%) of deep blue crystals, m.p. 236°.

Anal. Calcd. for C$_{14}$H$_{12}$Cl$_2$CoN$_4$: C, 45.92; H, 3.30; N, 15.30. Found: C, 45.73; H, 3.31; N, 15.59.

Dibromobis-(benzimidazole)-Co(II).—2.36 g. (0.02 mole) of benzimidazole in 8 ml. of absolute ethanol was added to 3.27 g. (0.01 mole) of CoBr$_2$·6H$_2$O in 4 ml. of absolute

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[16] See F. A. Cotton, D. M. L. Goodgame and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 4690 (1961) and the earlier literature cited therein.

ethanol. Deep blue crystals slowly formed. These were filtered, washed and dried *in vacuo*. Yield: 3.56 g. (78%), m.p. 251°.

Anal. Calcd. for $C_{14}H_{12}Br_2CoN_4$: C, 36.95; H, 2.66; N, 12.31. Found: C, 36.69; H, 2.56; N, 12.20.

Diiodobis-(benzimidazole)-cobalt(II).—2.36 g. (0.02 mole) of benzimidazole in 7 ml. of absolute ethanol was added to 3.13 g. (0.01 mole) of CoI_2 in 8 ml. of absolute ethanol. 30 ml. of chloroform was then added and the solution slowly evaporated in a partial vacuum until bluish-green crystals formed. These were filtered, washed and dried *in vacuo*. Yield: 2.37 g. (43%), m.p. 228°.

Anal. Calcd. for $C_{14}H_{12}CoI_2N_4$: C, 30.62; H, 2.20; N, 10.21. Found: C, 30.69; H, 2.43; N, 9.91.

Tetraethylammonium Tribromo-(benzimidazole)-cobaltate(II).—1.18 g. (0.01 mole) of benzimidazole in 4 ml. of absolute ethanol was added to 2.10 g. of (0.01 mole) tetraethylammonium bromide in 3 ml. of absolute ethanol. This mixture was heated and added to a hot solution of cobalt bromide (2.19 g., 0.01 mole) in 3 ml. absolute ethanol. A dark blue oil was formed, which solidified on cooling, and more needle-shaped crystals were formed. The solid was filtered, washed and dried *in vacuo*. Yield: 4.33 g. (79%), m.p., 143°.

Anal. Calcd. for $C_{15}H_{26}Br_3CoN_3$: C, 32.93; H, 4.79; N, 7.68. Found: C, 32.89; H, 5.02; N, 7.49.

Dinitratobis-(benzimidazole)-Co(II).—4.72 g. (0.04 mole) of benzimidazole in 25 ml. of absolute ethanol was added to 5.82 g. (0.02 mole) of cobalt nitrate hexahydrate in 5 ml. of absolute ethanol. The solution was slowly evaporated, when clusters of needle-like, deep magenta crystals formed. These were filtered off, washed and dried *in vacuo*. They were recrystallized by solution in ethylacetate and precipitation with benzene. Over-all yield, 2.7 gm. (32%), m.p., 167°.

Anal. Calc'd. for $C_{14}H_{12}CoN_6O_6$: C, 40.12; H, 2.89; N, 20.05. Found: C, 40.07; H, 2.86; N, 20.44.

Methyltriphenylarsonium Triiodo-(benzimidazole)-cobaltate(II).—3.13 g. (0.01 mole) of cobalt iodide in 1 ml. of acetone was mixed with 1.18 g. (0.01 mole) of benzimidazole in acetone, and the mixture was filtered. 4.48 g. (0.01 mole) of methyltriphenylarsonium iodide in 4 ml. of acetone was added, and the dark blue-green solution evaporated to about half bulk. On addition of 2 ml. of benzene, a blue-green precipitate was formed. This was filtered, washed and dried *in vacuo*. Yield: 7.72 g. (88%), m.p. 170°.

Anal. Calcd. for $C_{26}H_{24}AsCoI_3N_2$: C, 35.52; H, 2.75; N, 3.19. Found: C, 35.68; H, 2.77; N, 3.29.

Tetrakis-(benzimidazole)-cobalt(II) Perchlorate.—4.72 g. (0.04 mole) of benzimidazole, in 15 ml. of absolute ethanol, was added to 3.66 g. (0.01 mole) of cobalt perchlorate hexahydrate, in 5 ml. of absolute ethanol. The mixture was left to stand in a partially evacuated desiccator until crystals appeared. These were filtered off, washed with two very small quantities of absolute ethanol and dried *in vacuo*. These crystals appeared to contain two moles of ethanol.

Anal. Calcd. for $C_{32}H_{36}Cl_2CoN_8O_{10}$: C, 46.80; H, 4.42; N, 13.63. Found: C, 46.67; H, 4.37; N, 13.82.

The crystals were finely ground and exposed to air at room temperature for a few hours. The ethanol was given off, and a deep purple powder was left. Yield: 85%, m.p. 135°.

Anal. Calcd. for $C_{28}H_{24}Cl_2CoN_8O_8$: C, 46.04; H, 3.31; N, 15.34. Found: C, 46.12; H, 3.42; N, 15.19.

Measurement of Electrolytic Conductances.—Electrolytic conductance measurements were carried out using a Serfass bridge and a conventional cell, previously calibrated with an aqueous solution of potassium chloride. Results are recorded in Table I.

Magnetic Measurements.—These were carried out by the Gouy method, using a tube calibrated with $HgCo(NCS)_4$, as previously described.[16]

Measurements of Electronic Spectra.—Reflectance spectra were obtained using a Beckman DU spectrophotometer with a standard reflectance accessory. Magnesium carbonate was used as standard. All other spectra were obtained using a Cary model 14 recording spectrophotometer. The technique used for the mull spectra has been described previously.[16]

TABLE I

MOLAR CONDUCTANCES OF THE COMPLEXES

Compound	Molar conductance, 10^{-3} *M* in $C_6H_5NO_2$	CH_3NO_2	Temp., °C.
$[Co(C_7H_5N_2)_2]$	Insol.	Insol.	
$[CoCl_2(C_7H_6N_2)_2]$	<1 ohm^{-1}	....	25.2
$[CoBr_2(C_7H_6N_2)_2]$	<1 ohm^{-1}	....	25.4
$[CoI_2(C_7H_6N_2)_2]$	1.4	....	23.2
$[Co(NO_3)_2(C_7H_6N_2)_2]$	1.5	....	23.0
$[(C_2H_5)_4N][CoBr_3(C_7H_6N_2)]$	..	78.6 ohm^{-1}	23.9
$[CH_3(C_6H_5)_3As][CoI_3(C_7H_6N_2)]$	20.4	....	24.0
$[(C_7H_6N_2)_4Co](ClO_4)_2$	50.5	....	28.0

Discussion

The spectral and magnetic data for all of the complexes are collected in Tables II and III.

The benzimidazolato complex, $[Co(C_7H_5N_2)_2]$, is of particular interest. It seems reasonable to assume its structure to be that of an infinite polymer in which benzimidazole anions function as bidentate ligands forming bridges between cobalt ions, with each cobalt ion surrounded tetrahedrally by four nitrogen atoms. Such a structure is in accord with the formula and the insolubility of the compound and with the evidence from the spectrum and magnetic data that the cobalt is present in a tetrahedral environment.[16a] The unusually high value of the Weiss constant is consistent with the postulate that the Co(II) ions are connected by the relatively short symmetrical NCN chains which form part of a ring with a mobile system of pi electrons. Such a bridging system might well be expected to provide an effective path for superexchange coupling between Co(II) ions.

Using the spectral data for $[Co(C_7H_5N_2)_2]$, the value of Δ, the ligand field parameter, is found to be $\sim$5100 cm.$^{-1}$ while B, the Racah parameter is 716 cm^{-1}. These results were obtained by using the Tanabe and Sugano matrices as previously described[16] assigning ν_2 as 8700 cm.$^{-1}$ and ν_3 as 17,400 cm^{-1}. The Δ value is higher than any previously reported for a tetrahedral Co(II) complex.

It is interesting that in the compound $[Co(C_7H_6N_2)_4](ClO_4)_2$, the spectra show that the ligand field is here also very strong with Δ again about 5100 cm.$^{-1}$. A more precise estimate cannot be made because of the breadth of the spectral bands. These results thus show that the nitrogen atom or atoms of the imidazole ring make extremely effective contributions to the ligand fields in these complexes and, presumably then, in transition metal ion complexes generally. Thus the exceptional stability of many complexes containing ligands with imidazole rings may be in part due to exceptional ligand field stabilization effects.

From the magnetic moments (average, 4.27 ± 0.05 B.M.) and the Δ values of $\sim$5100 cm.$^{-1}$, the magnitude of the spin orbit coupling constants, λ' of cobalt in the two complexes $[Co(C_7H_5N_2)_2]$ and $[Co(C_7H_6N_2)_4]^{2+}$ are calculated[16] to be $\sim$128 cm^{-1}. This is somewhat below the range 140–170 cm.$^{-1}$ in which λ''s in other compounds have

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(16a) NOTE ADDED IN PROOF.—It has been shown recently by single-crystal X-ray study (I. Lindquist, private communication) that just this sort of structure occurs in the imidazole complex of Zn, $(C_3N_2H_3)_2Zn$.

TABLE II

SPECTRAL DATA FOR THE BENZIMIDAZOLE COMPLEXES

Compound	Medium	mμ	Cm.$^{-1}$	ε molar
[Co($C_7H_5N_2$)$_2$]	Reflectance	>1100	< 9,090	...
		~ 950(sh)	~10,530	...
		585	17,100	...
		~ 550(sh)	~18,200	...
	C_4Cl_6 mull	1150	8,700	...
		595	16,800	...
		~ 540(sh)	~18,520	...
[($C_7H_6N_2$)$_4$Co](ClO_4)$_2$	C_4Cl_6 mull	~1250(sh)	~ 8,000	...
		1150	8,700	...
		~1030(sh)	9,700	...
		Broad absorption		
		600–525	16,700–19,000	
	Acetone 0.001 *M*	~1200(sh)	8,330	...
		1110	9,009	66
		~1000(sh)	10,000	...
		575	17,400	645
		~ 538(sh)	~18,600	...
[$CoCl_2$($C_7H_6N_2$)$_2$]	Reflectance	>1100	< 9,090	...
		630	15,900	...
		~ 595(sh)	~16,800	...
	C_4Cl_6 mull	~1600(sh)	~ 6,250	...
		1350	7,410	...
		1100	9,090	...
		635	15,750	...
		~ 583(sh)	~17,150	...
		~ 510(sh)	~19,610	...
		~ 480(sh)	~20,830	...
		~ 435(sh)	~23,000	...
	Acetone 0.01 *M*	1620	6,170	69
		1430	6,990	72.5
		1080	9,260	51.5
	Acetone 0.001 *M*	632	15,820	612
		615	16,260	628
		580	17,240	400
[$CoBr_2$($C_7H_6N_2$)$_2$]	Reflectance	>1100	< 9,090	...
		650	15,400	...
		~ 615(sh)	~16,300	...
	C_4Cl_6 mull	1620	6,170	...
		1390	7,190	...
		1160	8,620	...
		657	15,220	...
		~ 625(sh)	~16,000	...
		597	16,750	...
		~ 525(sh)	~19,050	...
		~ 493(sh)	~20,300	...
		445	22,470	...
		430	23,260	...
	Acetone 0.01 *M*	~1650(sh)	~ 6,060	...
		1465	6,830	83
		1117	8,950	67
	Acetone 0.001 *M*	650	15,380	748
		630	15,870	712
		593	16,860	448
[CoI_2($C_7H_6N_2$)$_2$]	Reflectance	>1100	< 9,090	...
		~ 700(sh)	~14,300	...
		650	15,400	...
		~ 620(sh)	~16,130	...
	C_4Cl_6 mull	~1740(sh)	~ 5,750	...
		1450	6,900	...
		1160	8,620	...
		690	14,490	...
		656	15,240	...
		615	16,260	...

TABLE II (*Continued*)

Compound	Medium	mμ	Cm.$^{-1}$	ε molar
	Acetone 0.001 *M*	~1710(sh)	~ 5,850	...
		1500	6,670	55
		1165	8,580	52.5
		689	14,510	730
		656	15,240	840
		615	16,260	595
$[Co(NO_3)_2(C_7H_6N_2)_2]$	Reflectance	>1100	< 9,090	...
		750	13,330	...
		555	18,020	...
		~ 500(sh)	~20,000	...
	C_4Cl_6 mull	1370	7,300	...
		565	17,700	...
		~ 500(sh)	~20,000	...
	Acetone 0.01 *M*	1275	7,840	23.3
		1110	9,010	23
		725	13,790	12
		560	17,860	274
$[(C_2H_5)_4N][CoBr_3(C_7H_6N_2)]$	Reflectance	>1100	< 9,090	...
		690	14,490	...
	C_4Cl_6 mull	2090	4,785	...
		1500	6,670	...
		705	14,180	...
		675	14,810	...
		622	16,080	...
	Nitromethane 0.001 *M*	~1670(sh)	5,990	...
		1440	6,940	39
		687	14,560	720
		667	15,000	640
		~ 655(sh)	~15,270	...
		620	16,130	450
$[CH_3(C_6H_5)_3As][CoI_3(C_7H_6N_2)]$	Reflectance	>1100	< 9,090	...
		765	13,070	...
		705	14,180	...
		~ 660(sh)	~15,150	...
		~ 560(sh)	~17,860	...
		520	19,230	...
	C_4Cl_6 mull	1530	6,540	...
		760	13,160	...
		~ 725(sh)	~13,800	...
		697	14,350	...
		653	15,310	...
		~ 565(sh)	~17,700	...
		516	19,380	...
	Acetone 0.001 *M*	~1700(sh)	~ 5,880	...
		1505	6,650	56.5
		~1200(sh)	~ 8,330	...
		740	13,510	825
		~ 710(sh)	~14,100	...
		692	14,450	830
		658	15,200	625
		~ 616(sh)	~16,200	...

been found, but when the moments become low, the difference, $\mu_{obs} - 3.89$, to which λ' is proportional, becomes small and hence very sensitive to experimental error in μ_{obs}. In the present case an increase of 0.04 B.M., which is less than the expected experimental uncertainty of 0.05 B.M. would raise λ' to 140 cm^{-1}. Thus the apparent low value of λ' may not be of any significance.

It is noteworthy that cationic tetrahedral complexes of the divalent metal ions of the first transition series are quite rare. None, indeed, has been reported for any ion except Co(II), for which the $[Co(Ph_3PO)_4]^{2+}$, $[Co(Me_3PO)_4]^{2+}$ and $[Co(Ph_3AsO)_4]^{2+}$ ions have been studied spectrally and magnetically[16–18]; the $[Co(NH_3)_4]^{2+}$ ion also has been reported to occur in $[Co(NH_3)_4](ReO_4)_2$.[19]

The two compounds containing $[Co(C_7H_6N_2)X_3]^-$ (X = Br, I) ions are of interest in connection with the question of the cause of Weiss constants in the Curie–Weiss equations describing the temperature dependence of the susceptibilities

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[17] R. H. Holm and F. A. Cotton, *J. Chem. Phys.*, **32**, 1168 (1960).

[18] F. A. Cotton, D. M. L. Goodgame and M. Goodgame, to be published.

[19] K. S. Pitzer, *Z. Krist.*, **92**, 131 (1935).

TABLE III

MAGNETIC DATA FOR THE BENZIMIDAZOLE COMPLEXES

Compound	Temp., °K.	Correction × 10⁶, c.g.s.u. Diamagnetism	TIP[a]	χ_M^{corr} × 10⁶, c.g.s. units	μ, B.M.	θ, °K.
$[Co(C_7H_5N_2)_2]$	300	−142	410	6,872 ± 66		
	194.7			10,030 ± 15	4.27	−30
	74.5			21,660 ± 160		
$[(C_7H_6N_2)_4Co](ClO_4)_2$	300.2	−340	410	7,447 ± 125		
	195.0			11,270 ± 150	4.28	−8
	75.0			27,000 ± 980		
$[CoCl_2(C_7H_6N_2)_2]$	297.7	−194	500	8,145 ± 22		
	194.6			12,160 ± 110	4.48	− 9
	73.7			30,030 ± 450		
$[CoBr_2(C_7H_6N_2)_2]$	298.3	−214	500	8,156 ± 106		
	194.6			12,260 ± 58	4.50	− 9
	74.5			30,150 ± 800		
$[CoI_2(C_7H_6N_2)_2]$	296.5	−246	500	8,218 ± 27		
	194.5			12,330 ± 46	4.50	− 8
	73.7			30,600 ± 75		
$[Co(NO_3)_2(C_7H_6N_2)_2]$	296.7	−182	500	8,477 ± 109		
	194.5			12,910 ± 133	4.56	− 7
	73.2			31,700 ± 333		
$[(C_2H_5)_4N][CoBr_3(C_7H_6N_2)]$	299.5	−286	500	8,474 ± 34		
	194.7			12,620 ± 36	4.55	− 7
	74.0			31,683 ± 37		
$[CH_3(C_6H_5)_3As][CoI_3(C_7H_6N_2)]$	299.0	−425	500	9,044 ± 3		
	194.8			13,440 ± 88	4.71	− 8
	74.2			33,720 ± 300		

[a] TIP = temperature-independent paramagnetism, *cf.* ref. 16 and 20.

of tetrahedral Co(II) complexes. Two possible causes of the Weiss constants are intermolecular antiferromagnetic interactions and, as Figgis pointed out, distortions of the tetrahedral symmetry of the ligand field.[20] Since the order of the ligands concerned in the spectrochemical series is $I^- < Br^- < C_7H_6N_2$, the $[Co(C_7H_6N_2)I_3]^-$ ion must have a greater trigonal component in the ligand field than does $[Co(C_7H_6N_2)Br_3]^-$. According to the theory given by Figgis, this will cause the Weiss constant to be greater in the iodo complex than it is in the bromo one. Our observations do not reveal any significant difference between the two. In the corresponding $[Co(Ph_3P)X_3]^-$ complexes, a difference of about 5° in the proper direction was found.[21]

The spectral and magnetic data for the $[CoX_3(C_7H_6N_2)]^-$ ions are otherwise in excellent agreement with theoretical expectation. While the spectral bands, ν_2 and ν_3, are so greatly split and so broad that any attempt to assign to them single energy values and then to calculate Δ and B' values would be of questionable validity, cruder comparisons can be shown to give satisfactory results. Thus the ν_2 absorption of $[CoBr_3(C_7H_6N_2)]^-$ is approximately 5% higher in energy than for $[CoI_3(C_7H_6N_2)]^-$ which is consistent with the fact[16] that ν_2 is about 8% higher in $[CoBr_4]^{2-}$ than in $[CoI_4]^{2-}$. In addition, for each of the $[CoX_3(C_7H_6N_2)]^-$ ions the ν_2 bands are shifted ~30% of the distance between those for the corresponding $[CoX_4]^{2-}$ ions and the ν_2 band of $[Co(C_7H_6N_2)_4]^{2+}$ discussed above. Thus, while the greater asymmetry of the ligand fields contributes to broadening and splitting of the bands, the approximate energy centers behave as expected on the hypothesis of an averaged ligand field. The magnetic moments for the $[CoX_3(C_7H_6N_2)]^-$ ions are also in the order expected from theory[16] using the above mentioned spectral data and assuming that the effective value of the spin–orbit coupling constant is not significantly different in the two complexes.

For the $[CoX_2(C_7H_6N_2)]$ complexes in which X represents the halide ions, Cl^-, Br^- and I^-, the spectral data are again in agreement with the relative positions of the ligands in the spectrochemical series. However, the bands are very broad and severely split and the differences in band energies among the three compounds is not large or well-defined. Thus the spectral data would lead us to expect only small differences in the magnetic moments, and in fact the differences are apparently less than ~0.12 B.M. between the chloro and iodo compounds since allowing for an experimental uncertainty of ~0.05 B.M. in each moment, the minimum value for $[CoCl_2(C_7H_6N_2)_2]$ would be 4.43 B.M. and the maximum value for $[CoI_2(C_7H_6N_2)_2]$ would be 4.55 B.M.

This low sensitivity of the energy level separations and, hence, of the magnetic moments of the $[CoX_2(C_7H_6N_2)_2]$ compounds to variation in the halide ions is a natural consequence of the fact that the halide ions in these complexes contribute relatively little (~ 35%) to the total ligand field,[22]

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(20) B. N. Figgis, *Trans. Faraday Soc.*, **56**, 1553 (1960).

(21) F. A. Cotton, O. D. Faut, D. M. L. Goodgame and R. H. Holm, *J. Am. Chem. Soc.*, **83**, 1780 (1961).

(22) We are not unaware of the crudity of this argument, but it seems to us that it must be essentially correct and it does provide a simple explanation for the facts.

and therefore small variations in this small contribution have a very minor effect upon the total field strength. Conversely, the increase from one to two benzimidazole ligands in going from the $[CoX_3(C_7H_6N_2)]^-$ to $[CoX_2(C_7H_6N_2)_2]$ complexes has a very marked effect on both the spectra and the magnetic moments.

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Rates of Some Substitution Reactions of Platinum(II) Complexes

BY HARRY B. GRAY[1]

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Rates of replacement of halide by different ligands in platinum(II) complexes of the type $[Pt(dien)(halide)]^+$ are reported.[2] The results show that both first order and second order reactions occur. The mechanisms which may lead to the first and second order rate laws are discussed. The bimolecular reactivities of different incoming ligands in reactions of platinum complexes decrease in the order

$$SC(NH_2)_2 \approx CNS^- \approx I^- > N_3^- \approx NO_2^- > py \approx NH_3 \approx Br^- > Cl^- > H_2O > OH^- \approx NH_2CH_2COOH$$

which is also approximately the order of decreasing *trans*-effect of these ligands. The relative reactivities of Cl^- and NO_2^- in reactions of different platinum(II) complexes vary strikingly with the charge on the complex, and this is interpreted in terms of the electronic features of a possible reaction mechanism.

Introduction

In previous papers[3,4] it has been suggested that a general rate law for ligand substitutions in square planar metal complexes is

$$\text{Rate} = \{k_1 + k_2[Y]\}\ [\text{complex}] \qquad (1)$$

where k_1 and k_2 are first and second order rate constants, respectively, and Y is the entering group. This form of rate law was first "discovered" in square planar reactions by Rich and Taube[5] for the exchange of $^{36}Cl^-$ with $AuCl_4^-$ and more recently by Martin[6] for *trans*-$Pt(NH_3)_2Cl_2$-$^{36}Cl^-$ exchange, and Basolo, *et al.*,[3,4] for reactions of platinum(II), palladium(II) and nickel(II) complexes with pyridine in water or ethanol solution. Also, although not specifically mentioned at the time, all previous work on square planar kinetics is consistent with this form of rate law.[7]

This present study will show that eq. 1 is valid for reactions of platinum(II) complexes in water solution with a number of different reagents. The reaction studied is the replacement of a halide ligand in complexes of the type $Pt(dien)X^+$, *viz.*

$$Pt(dien)X^+ + Y^- \longrightarrow Pt(dien)Y^+ + X^- \qquad (2)$$

The mechanisms which can account for k_1 and k_2 will also be discussed.

Experimental

A. Preparation and Purification of Materials.—The [Pt(dien)X] X and [Pt(dien)X] NO_3 complexes used in this study had been prepared previously following methods described in the literature. Other minor preparatory details and the analyses have been given.[3]

Reagent grade pyridine was dried with KOH and distilled, b.p. 114°: other materials used were reagent grade.

Sodium hydroxide solutions were prepared using distilled water which had previously been boiled and flushed with nitrogen to remove CO_2. The NaOH concentrations were checked by conductivity measurements.

B. Determination of Reaction Rates. (1) Conductance Method.—Reactions studied by this method were the following

$$Pt(dien)Br^+ + SC(NH_2)_2 \longrightarrow Pt(dien)\{SC(NH_2)_2\}^{2+} + Br^- \qquad (3)$$

$$Pt(dien)X^+ + OH^- \longrightarrow Pt(dien)OH^+ + X^- \qquad (4)$$

The conductivity of aqueous solutions of the complexes corresponded to 1:1 electrolytes and did not change with time. Thus no net hydrolysis occurred, *e.g.*

$$Pt(dien)X^+ + H_2O \nrightarrow Pt(dien)H_2O^{2+} + X^- \qquad (5)$$

Standard aqueous solutions of complex and reactant were thermostated in a Y-shaped conductance cell and, after the desired temperature was reached, were mixed by tipping the cell. Complete concentration data for these reactions are given in Table I. At the concentrations used both reactions 3 and 4 went to completion as judged by the total conductance changes observed.[8] The completeness of reaction 4 as well as the rate constants were checked spectroscopically as discussed in the next section. Pseudo first order rate constants were evaluated as described earlier[9] and are given in Table I.

Reaction 3 is shown to depend on the concentration of thiourea, and at low thiourea concentrations first order behavior was not observed for the complete reaction. This is expected since there is an appreciable thiourea concentration change during the course of the reaction. The values of the pseudo first order rate constants in these cases were obtained by graphing only the data for the first 25% of reaction.

(2) Spectrophotometric Method.—Reactions studied by this method were

$$Pt(dien)Cl^+ + Y^- \rightleftharpoons Pt(dien)Y^+ + Cl^- \qquad (6)$$
$$(Y^- = Br^- \text{ or } I^-)$$

$$Pt(dien)Br^+ + Y^- \rightleftharpoons Pt(dien)Y^+ + Br^- \qquad (7)$$
$$(Y^- = Cl^-, I^-, NO_2^-, CNS^- \text{ or } N_3^-)$$

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(2) Abbreviations used in this paper: dien = diethylenetriamine, py = pyridine, X^- = halide.

(3) F. Basolo, H. B. Gray and R. G. Pearson, *J. Am. Chem. Soc.*, **82**, 4200 (1960).

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(6) D. S. Martin, Jr., and R. J. Adams, "Advances in the Chemistry of the Coordination Compounds," Macmillan Co., New York, N. Y., 1961, pp. 579-589.

(7) (a) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 172-212; (b) A. A. Grinberg, *Russian J. Inorg. Chem.*, **4**, 139 (1959); (c) More recent articles are cited in ref. 3.

(8) In reaction 3 the molar conductance of $Pt(dien)\{SC(NH_2)_2\}^{2+}$ is assumed to be two times that of $Pt(dien)X^+$.

(9) D. Banerjea, F. Basolo and R. G. Pearson, *J. Am. Chem. Soc.*, **79**, 4055 (1957).