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Oxidative Addition of Halogens and Pseudohalogens to Dihalo(1,10-phenanthroline)platinum(II)

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When platinum(II) complexes Pt(phen)X_2 (phen = 1,10-phenanthroline, X = Cl, Br, and I) are treated with oxidizing agents, AB, platinum(IV) complexes Pt(phen)X_2AB are obtained. Oxidizing agents include Cl_2, Br_2, I_2, ICl, ICN, $(SCN)_2$, and NOCl, while $(CN)_2$, BrCN, $S(CN)_2$, H_2O_2, CH_3I, $C_6H_5CH_2Cl$, and $(CH_3)_2S_2$ are unreactive at temperatures up to 100°. With excess iodine, Pt(phen)X_2 complexes are oxidized to platinum(IV) compounds that contain triiodide ligands. In the presence of a great excess of a nonoxidizing ligand, the ligand can be added in preference to part of the oxidizing agent. For products containing chloride ligands, the infrared spectra indicate that the addition has been to trans positions in the complex.

Introduction

Oxidative addition reactions of the d^8 transition metal complexes have produced a number of interesting new compounds. Oxidation of platinum(II) to platinum(IV) with addition of the oxidant was reported in the nineteenth century,[1] but although it is one of the most familiar d^8 ions, platinum(II) has received relatively little attention during the recent renewal of interest in these reactions. Oxidizing agents have been confined to chlorine, bromine, methyl iodide, hydrogen chloride, and hydrogen peroxide.[2]

Two factors have prompted us to extend the application of these reactions for platinum(II). First, some novel reagents have recently been investigated, including the use of $(SCN)_2$ in reactions of palladium(II).[3] The second factor was a mechanistic study of the platinum(II) oxidative addition reaction by Jones and Morgan,[4] in which the oxidation of $Pt(CN)_4^{2-}$ by Cl_2 and Br_2 was found initially to give an oxidized complex of platinum containing only one halogen atom. The second halide ligand appeared in the final product as the result of a subsequent substitution step. The mechanism suggested the synthetically interesting possibility of adding ligands in the course of the oxidation reaction that were not part of the oxidizing agent. For example, although BrCl is not available as a reagent, addition of Br and Cl might be effected by bromine oxidation in the presence of chloride ions. Other unsymmetrical additions might be obtained by using unsymmetrical reagents such as $S(CN)_2$ or ICl. This paper reports attempts at oxidative addition to Pt(phen)X_2 (phen = 1,10-phenanthroline; X = Cl, Br, I) using halogens and pseudohalogens.

Experimental Section

Chemicals. Dichloro(phenanthroline)platinum(II), Pt(phen)Cl_2, was prepared by boiling a solution of K_2PtCl_4[5] (1.0 g) and 1,10-phenanthroline (0.5 g) in 1.5 l. of water containing 0.5 ml of HCl. After 20 hr, the reaction mixture was allowed to cool to room temperature, and the light yellow product that had precipitated was filtered out, washed with hot water, and dried under vacuum; yield 1.04 g (97%). Dibromo(phenanthroline)platinum(II), Pt(phen)Br_2, was prepared in a similar manner from K_2PtBr_4[5] (1.0 g), phenanthroline (0.33 g), KBr (10 g), and HBr (0.5 ml). The yellow product was dried at 110° for 20 hr; yield 0.79 g (88%). To prepare diiodo(phenanthroline)platinum(II), Pt(phen)I_2, a solution of K_2PtCl_4 (1.0 g) and KI (200 g) in 200 ml of water was heated to boiling and allowed to stand for several days. It was then added to a solution of phenanthroline (0.48 g) in 2.8 l. of water. After the reaction mixture had been boiled for 1 day, dark yellow Pt(phen)I_2·H_2O was filtered out, washed with water, and dehydrated by heating to 100° for 1 day; yield 1.36 g (90%).

Most of the platinum(IV) compounds were prepared by variations on a single procedure. A fine slurry was made of the Pt(phen)X_2 compound in the solvent, usually chloroform. The oxidizing agent was added in another portion of solvent. When reaction was complete, the solid product was filtered out, washed thoroughly with solvent, and dried. *Caution*! The oxidizing agents are toxic and volatile. Operations with them should be carried out in a good hood, and appropriate provision should be made for disposal of filtrates from the reaction mixtures. Solid thiocyanogen is reported to polymerize explosively, so care should be exercised in concentrating solutions of this reagent.

Reactions of Chlorine. Tetrachloro(phenanthroline)platinum(IV), Pt(phen)Cl_4. Chlorine was bubbled into a well-stirred suspension of Pt(phen)Cl_2 (0.04 g) in 75 ml of $CHCl_3$ for 10 min. After an additional 10 min of stirring, the light yellow product was filtered out and dried at 105°; yield 0.45 g (94%).

***cis*-Dibromodichloro(phenanthroline)platinum(IV), Pt(phen)Br_2Cl_2.**[6] Chlorine-saturated $CHCl_3$ (20 ml) was added to Pt(phen)Br_2 (0.30 g) in 60 ml of $CHCl_3$, both reagents being ice cold. The mixture was stirred vigorously for 2 min, and the yellow product was filtered out and dried under vacuum; yield 0.20 g (59%). Oxidation of Pt(phen)I_2 with Cl_2 under a variety of conditions always resulted in some replacement of iodide by chloride.

Reactions of Bromine. *trans*-Dibromodichloro(phenanthroline)platinum(IV), Pt(phen)Cl_2Br_2. Pt(phen)Cl_2 (0.49 g) was treated with Br_2 (2 g) in 200 ml of refluxing $CHCl_3$ for 20 min. The yellow product was dried at 105° for 20 hr; yield 0.69 g (90%). The same material was obtained in 95% yield when the reaction was carried out in 400 ml of boiling water containing 2 ml of HBr.

Tetrabromo(phenanthroline)platinum(IV), Pt(phen)Br_4. A mixture of Pt(phen)Br_2 (0.37 g), Br_2 (0.5 g), and 75 ml of $CHCl_3$ was heated briefly to boiling, giving an orange solid which was dried at 105° for 48 hr; yield 0.47 g (95%). Like chlorine, bromine reacted with Pt(phen)I_2 both to oxidize the platinum and to replace some of the iodide.

1,2,3-Tribromochloro(phenanthroline)platinum(IV), Pt(phen)Br_3Cl. Pt(phen)Br_2 (1.0 g) was treated with Br_2 (4.0 g) in boiling 8 *M* HCl for 20 min. The yellow product was dried at 105°.

Reactions of Iodine. *cis*-Dichlorobis(triiodo)(phenanthroline)platinum(IV), Pt(phen)$Cl_2(I_3)_2$.[7] Pt(phen)Cl_2 (0.20 g) was treated overnight with iodine (1.5 g) in 80 ml of refluxing chloroform. The black product was dried under vacuum; yield 0.50 g (92%).

***cis*-Dibromoiodo(triiodo)(phenanthroline)platinum(IV), Pt(phen)$Br_2I(I_3)$.** Pt(phen)Br_2 (0.10 g) was treated for 15 min with I_2 (0.5 g) in 50 ml of refluxing $CHCl_3$. The resulting black solid was dried under vacuum; yield 0.15 g (77%).

Tetraiodo(phenanthroline)platinum(IV), Pt(phen)I_4. A solution of I_2 (0.404 g) in 20 ml of $CHCl_3$ was added dropwise over a period of 2 hr to a suspension of Pt(phen)I_2 (1.00 g) in 75 ml of boiling $CHCl_3$. The reaction mixture was filtered while hot, and the black product was dried under vacuum; yield 1.25 g (89%). The X-ray powder pattern of this compound was compared with those of Pt(phen)I_2 and Pt(phen)$I_3(I_3)$; no common lines were observed.

1,2,3-Triiodo(triiodo)(phenanthroline)platinum(IV), Pt(phen)$I_3(I_3)$. A mixture comprising Pt(phen)I_2 (0.31 g), I_2 (0.8 g), and 50 ml of $CHCl_3$ was boiled for 15 min. The resulting black solid was dried under vacuum; yield 0.49 g (87%). When 140 mg of this product was heated at 103° for 3 days, it turned yellow and its weight decreased by 62 mg (predicted for reversion to Pt(phen)I_2, 60 mg). Pt(phen)$I_3(I_3)$ was also obtained from the treatment of Pt(phen)I_2 with I_2 in concentrated HCl and by treatment of Pt(phen)I_4 with I_2 in $CHCl_3$.

Reactions of Iodine Monochloride. 1,2,3-Trichloroiodo(phenanthroline)platinum(IV), Pt(phen)Cl_3I. Pt(phen)Cl_2 (0.30 g) was

Table I. Analytical Data

		% C		% H		% N		% Pt		% Cl		% Br		% I	
Compd	Color	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
Pt(phen)Cl_2[a]	Lt yellow	32.3	32.2	1.79	1.85			43.7	43.9						
Pt(phen)Br_2	Yellow	26.9	26.8	1.50	1.83	5.23	5.31	36.4	36.2			29.9	30.2		
Pt(phen)I_2	Dk yellow	22.9	22.7	1.25	1.32	4.38	4.56	31.0	30.9					39.7	39.8
Pt(phen)Cl_4	Lt yellow	27.9	28.0	1.70	1.84	5.42	5.29	37.7	37.5	27.5	27.7				
Pt(phen)Br_2Cl_2	Yellow	23.8	23.6	1.32	1.51	4.62	4.46	32.2	32.3	11.7	11.8	26.4	26.3		
Pt(phen)Cl_2Br_2	Yellow	32.2	31.9	1.32	1.51	4.62	4.60	32.2	31.9	11.7	11.7	26.4	26.5		
Pt(phen)Br_4	Orange	20.7	21.0	1.15	1.29	4.03	4.13	28.1	28.0			46.0	46.0		
Pt(phen)$Cl_2(I_3)_2$	Black	11.9	12.0	0.67	0.67	2.32	2.26	16.2	16.2	5.87	5.87			63.0	62.9
Pt(phen)$Br_2I(I_3)$	Black	13.8	14.0	0.77	0.83	2.69	2.57	18.7	18.8			15.3	15.1	48.7	48.8
Pt(phen)I_4	Black	16.3	16.4	0.91	0.94	3.18	3.03	22.1	21.9					57.6	57.3
Pt(phen)$I_3(I_3)$	Black	12.7	12.5	0.70	0.75	2.46	2.25	17.2	17.2					67.1	67.0
Pt(phen)Br_3Cl	Yellow	22.1	22.1	1.23	1.24	4.30	4.43	30.0	29.7	5.45	5.43			36.9	36.6
Pt(phen)Br_2ICl	Brown-orange	20.7	21.0	1.15	1.38	4.02	3.98	27.9	27.7	5.08	4.92	22.9	23.0	18.2	18.2
Pt(phen)Cl_3I	Orange	23.7	23.9	1.31	1.41	4.61	4.79	32.1	32.1	17.5	17.5			20.9	21.1
Pt(phen)I_3CN	Red-brown	20.0	20.4	0.98	1.07	5.50	5.62	24.9	24.8					48.7	48.4
Pt(phen)$Cl_2(SCN)_2$	Orange	29.9	30.1	1.42	1.61	10.0	10.2	34.7	34.4	12.6	12.8				
Pt(phen)$Br_2(SCN)_2$	Orange	25.8	25.9	0.23	1.49	8.60	8.38	30.0	30.0			24.6	24.3		
Pt(phen)ICl_3	Brown	23.7	23.7	1.31	1.15	4.61	4.36	32.1	32.3	17.5	17.3			20.9	20.9
Pt(phen)I_3Cl	Red-brown	18.2	18.0	1.01	1.21	3.54	3.31	24.6	24.6	4.48	4.51			48.2	47.6

[a] phen = $C_{12}H_8N_2$.

stirred with ICl[8] (0.12 g) in 100 ml of $CHCl_3$. The reaction was allowed to proceed for 15 min in a salt–ice bath and for another 15 min without cooling. The orange product was dried at 60° under vacuum for 20 hr; yield 0.34 g (83%).

***cis*-Dibromochloroiodo(phenanthroline)platinum(IV), Pt(phen)-Br_2ICl.** A solution of ICl (0.13 g) in 50 ml of $CHCl_3$ cooled to −10° was slowly added to a slurry of Pt(phen)Br_2 in 50 ml of $CHCl_3$ at the same temperature. After 15 min, a brown-orange product was isolated and dried at 60° under vacuum; yield 0.48 g (95%).

Chlorotriiodo(phenanthroline)platinum(IV), Pt(phen)I_3Cl. Pt-(phen)I_2 (0.53 g) was treated with ICl and the reaction was allowed to proceed for 1 min. The red-brown product was filtered out, washed with $CHCl_3$, and dried under vacuum; yield 0.59 g (89%).

Reactions of Cyanogen and Its Halogen Derivatives. 1,2,3-Triiodocyano(phenanthroline)platinum(IV), Pt(phen)I_3CN. The red-brown product was obtained by the reaction of Pt(phen)I_2 (0.80 g) with ICN[9] (0.8 g) in 75 ml of boiling $CHCl_3$ for 5 hr. It was dried under vacuum; yield 0.23 g (93%). Pt(phen)Cl_2 and Pt(phen)Br_2 were treated with ICN for several days in refluxing $CHCl_3$. Platinum analysis indicated little or no conversion to the desired platinum(IV) compounds. After treatment with BrCN for several days in boiling $CHCl_3$ or H_2O, Pt(phen)I_2 was recovered unchanged. Cyanogen was similarly unreactive.

Reactions of Thiocyanogen. *cis*-Dichlorodithiocyanato(phenanthroline)platinum(IV), Pt(phen)$Cl_2(SCN)_2$. Silver thiocyanate (3.4 g) was suspended in 40 ml of $CHCl_3$ at 5°. A solution of Br_2 (1.6 g) in 10 ml of $CHCl_3$ was added, and the mixture was stirred for 1 hr and filtered. Pt(phen)Cl_2 (0.3 g) was added to the filtrate. After 30 min, the orange solid was isolated and dried at 100° under vacuum; yield 0.20 g (53%).

***cis*-Dibromodithiocyanato(phenanthroline)platinum(IV), Pt-(phen)$Br_2(SCN)_2$.** Similar treatment of Pt(phen)Br_2 (0.30 g) for 30 min gave an orange solid that was dried under vacuum at room temperature; yield 0.18 g (49%). Thiocyanogen reacted rapidly with Pt(phen)I_2 to give a brown solution from which no identifiable platinum(IV) compound was isolated.

Reactions of Nitrosyl Chloride. 1,2,6-Trichloroiodo(phenanthroline)platinum(IV), Pt(phen)ICl_3. Nitrosyl chloride was bubbled into a slurry of Pt(phen)I_2 (0.2 g) in refluxing $CHCl_3$ for 0.5 hr. The brown product was dried at 103° in air for 2 hr; yield 0.15 g (78%). A similar reaction using Pt(phen)Cl_2 gave Pt(phen)Cl_4. *Anal.* Calcd for Pt(phen)Cl_4: Pt, 37.7. Found: Pt, 37.4. With Pt(phen)Br_2, Pt(phen)Br_2Cl_2 was obtained. *Anal.* Calcd for Pt(phen)Br_2Cl_2: Pt, 32.1. Found: 31.9. Nitrosyl chloride reacted with platinum compounds at lower temperatures to give products the infrared spectra of which indicated that they contained bound NO. Pure compounds of this kind have not yet been obtained.

Other Reagents. The platinum(II) compounds were treated with CH_3I, $C_6H_5CH_2Cl$, $(CH_3)_2S_2$, H_2O_2, and $S(CN)_2$, under a variety of conditions. Judging by the platinum analyses of the solids isolated from the reaction mixtures, the platinum did not undergo oxidation with these reagents.

Quantitative analyses for platinum were done by ignition. Analyses for other elements were carried out by Huffman Laboratories, Inc., Wheatridge, Colo. The results are given in Table I.

Infrared spectra were recorded on a Beckman IR12 spectrophotometer. Samples were suspended in Nujol for measurements between 200 and 300 cm^{-1} and were prepared as KBr disks for spectra above 300 cm^{-1}. X-Ray powder patterns were observed with Cu Kα radiation with a Debye–Scherrer powder camera (radius 57.3 mm). Ultraviolet spectra were recorded on a Cary 14 spectrophotometer.

Results and Discussion

The treatment of platinum(II) compounds Pt(phen)X_2 (X = Cl, Br, I) with an oxidizing agent AB gave the normal product in most cases, a platinum(IV) compound Pt(phen)-X_2AB with A and B trans to each other. Some reagents, notably CH_3I, $C_6H_5CH_2Cl$, $(CH_3)_2S_2$, H_2O_2, and $S(CN)_2$, did not oxidize platinum(II). Under certain circumstances oxidation occurred without addition of the oxidizing agent or with only partial addition.

Among halogen oxidizing agents, chlorine and bromine added normally to the chloride and bromide complexes but also oxidized the iodide ligands of Pt(phen)I_2. Iodine gave unanticipated products, some of which can be rationalized using the reaction mechanism of Jones and Morgan.[4] With the iodide complex as the starting material, iodine gave a product that we formulate as $Pt(phen)I_3(I_3)$. The mechanism predicts that the initial oxidation product would be $Pt(phen)I_3(solvent)^+$ and I^-. Because I_2 was present in excess, free I^- would have been converted into triiodide, and this ion could have been the one to displace the solvent ligand, giving $Pt(phen)I_3(I_3)$. Analogous results were obtained with $Pt(phen)Br_2$, but $Pt(phen)Cl_2$ gave $Pt(phen)Cl_2(I_3)_2$. Since triiodide ligands are rare in transition metal complexes (two are known for platinum: $(C_5H_5N)_2Pt(C_3H_5)_2(I_3)_2$ and $[(C_6H_5)_3P]_2Pt(CH_3)(I_3))$,[10] we sought another formulation for these complexes. The most appealing alternative involved a charge-transfer complex between I_2 and the π-electron cloud of the phenanthroline, similar to the interaction between bromine and benzene.[11] As a test of this hypothesis, $Pt(phen)Cl_4$ was treated with I_2. This complex was chosen because $Pt(phen)Cl_2$ appeared to have the greatest affinity for triiodide and because the possibility of forming a ClI_2^- ligand seemed remote. After treatment, the complex was recovered unchanged, probably ruling out a charge-transfer complex as well as iodine addition to phenanthroline. When a stoichiometric amount of I_2 was slowly added to a heated slurry of $Pt(phen)I_2$ (in order to prevent any accumulation of I_2 which could form I_3^-), a black compound of the composition $Pt(phen)I_4$ was obtained. X-Ray powder patterns indicated that this was not an equimolar mixture of $Pt(phen)I_2$ and $Pt(phen)I_3(I_3)$. Treatment of $Pt(phen)I_4$ with excess I_2 gave $Pt(phen)I_3(I_3)$. This result can be interpreted as involving the conversion of an iodide ligand to a triiodide ligand or as indicating that the starting material was a platinum(II)–platinum(IV) compound such as $[Pt(phen)I_2][Pt(phen)I_3(I_3)]$, perhaps having a structure resembling that of $Pt(en)Br_3$.[12] In an effort to understand the nature of these compounds, their ultraviolet and photoelectron spectra were examined. Triiodide ion has absorption maxima at 365 and 295 mμ,[13] and the ligand is reported to have maxima at the same wavelengths.[10] None of our compounds exhibited these absorptions. A possible explanation of this discrepancy is that in the work of Kistner, *et al.*, the solutions of $(C_5H_5N)_2Pt(C_3H_5)_2(I_3)_2$ on which measurements were made contained ionized triiodide, displaced from the coordination sphere of platinum(IV) by solvent molecules. What is demonstrated in ref 10 is that some form of triiodide is present and that in dimethyl sulfoxide solution the allyl groups are σ bonded.

One of the reactions which was successful in adding a ligand that was not part of the oxidizing agent was that of $Pt(phen)Br_2$ with Br_2 in hot 8 *M* HCl. The product, $Pt(phen)Br_3Cl$, had the chloro ligand in the axial position (*i.e.*, not trans to phenanthroline), as demonstrated by the infrared spectrum discussed below. Although this is the product predicted by the mechanism,[4] an argument could be made that it had $Pt(phen)Br_4$ as a precursor and was formed either by simple substitution or by a platinum(II)-catalyzed route. Some similar attempts failed, either because the ligand in excess attacked the starting material, as with Br_2 and SCN^- with $Pt(phen)Br_2$ (which appeared to give $Pt(phen)(SCN)_2$), or because the ligand in excess did not successfully compete with the ligand produced by oxidation, as when $Pt(phen)I_2$ was treated with I_2 and excess Cl^-, giving $Pt(phen)I_3(I_3)$).

Unsymmetrical additions were also observed with reagents such as ICl and ICN. Infrared spectra showed that the ICl additions did not give equimolar mixtures of diiodo and dichloro complexes. ICN was among the least active reagents for which reaction was obtained. It added completely only to $Pt(phen)I_2$ and gave a small amount of addition on extended treatment of $Pt(phen)Br_2$ and no reaction with $Pt(phen)Cl_2$. This was the general order of reactivity based on the qualitative observation that the iodo complex was the most reactive and the chloro complex the least. Neither BrCN nor $(CN)_2$ would add to $Pt(phen)I_2$, indicating that simple oxidizing power is not the only factor in this reaction, since $(CN)_2$ will oxidize Br^- and I^-.

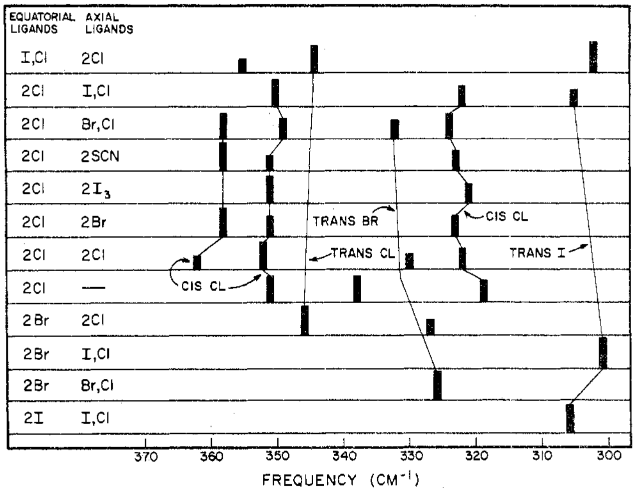

Figure 1. Schematic diagram of the infrared spectra (400–300 cm^{-1}) of compounds containing Pt–Cl bonds.

Thiocyanogen, $(SCN)_2$, added smoothly to the chloride and bromide complexes to give dithiocyanato complexes. The mode of bonding of thiocyanato ligands may be determined by the frequency of the CN stretching frequency in the infrared spectrum.[14] S- and N-bonded ligands have ν(CN) respectively above and below 2100 cm^{-1}. $Pt(phen)X_2(SCN)_2$ exhibited a strong absorption at 2129 cm^{-1} for X = Cl and 2119 cm^{-1} for X = Br. The 2000–2100-cm^{-1} region contained no absorptions. In the NCS bending region, new absorptions arose for both compounds at 407 cm^{-1} (strong) and 455 cm^{-1} (medium). In the CS stretching region, weak absorptions appeared at 795 and 819 cm^{-1}, the latter probably being the first overtone of δ(SCN).[15] These data are all consistent with the expected M–S mode of binding. A strong absorption, perhaps ν(M–S), also appeared at 286 cm^{-1}.

The infrared spectra of the Pt–Cl stretching region are represented schematically in Figure 1 for the complexes containing chloro ligands. This region was transparent for other complexes. The spectra are consistent with additions of the oxidizing agents at the axial positions in the complexes (*i.e.*, not in the same plane as the phenanthroline).

In common with $Pt(phen)Cl_2$, all the complexes derived from it have an absorption at 319–324 cm^{-1} and another at 349–352 cm^{-1}. $Pt(phen)Cl_2$ has a third absorption at 338 cm^{-1}, which in its derivatives seems to have shifted to the 358–362-cm^{-1} region. $Pt(phen)Cl_3I$ and $Pt(phen)Cl_2(I_3)_2$ do not exhibit the third band, but both have a very strong absorption around 359 cm^{-1} that obscures this region.

The frequency of the axial chloride stretch is a sensitive function of the ligand trans to it. Compounds with axial chlorides trans to iodides, $Pt(phen)I_3Cl$, $Pt(phen)Br_2ICl$, and $Pt(phen)Cl_3I$, have an absorption at 301–306 cm^{-1}. Those with chloride trans to bromide, $Pt(phen)Br_3Cl$ and $Pt(phen)Cl_3Br$, absorb at 326 and 332 cm^{-1}, respectively. Finally *trans*-dichloro complexes exhibit an absorption at about 345 cm^{-1} (for $Pt(phen)Cl_4$, this region is obscured by the very strong absorption caused by the equatorial chlorides). A third, weak absorption occurs for all the *trans*-dichloro complexes: at 327, 355, and 330 cm^{-1}, for $Pt(phen)Br_2Cl_2$, $Pt(phen)ICl_3$, and $Pt(phen)Cl_4$, respectively. The only absorption in Figure 1 that remains to be accounted for is the one at 303 cm^{-1} in the spectrum of $Pt(phen)ICl_3$. This compound, derived from $Pt(phen)I_2$, is unique in having two different equatorial halides, and it seems reasonable to assign the 303-cm^{-1} band to the stretching mode of the equatorial chloride cis to the iodide. The geometries of the chloride complexes indicate that oxidative addition reactions have produced trans products, that the rearrangement of ligands in the original complexes has not occurred (although one case of substitution was observed), and that the products are not necessarily the thermodynamically stable ones (since two pairs of isomers, $Pt(phen)Cl_2Br_2$, $Pt(phen)Br_2Cl_2$ and $Pt(phen)Cl_3I$, $Pt(phen)ICl_3$, were obtained).

The infrared spectra presented a more complicated aspect in the Pt–Br stretching region, 200–300 cm^{-1}. All of the complexes absorbed in this range. Inspection of the spectra revealed that bromide-containing compounds have some absorptions at frequencies where compounds not containing bromide did not absorb. $Pt(phen)Br_2$ and its derivatives had absorptions at 213–215, 245–249, and 260–265 cm^{-1}, the sole exception being $Pt(phen)Br_2$, for which the intermediate frequency was absent. Noting the parallel with the equatorial chloride vibrations 100 cm^{-1} higher, we expect the third absorption in the platinum(II) compound should lie near 238 cm^{-1}. In fact the strongest absorption in the spectrum of the compound lies at 239 cm^{-1}.

Compounds with axial bromide(s) absorbed at 201–210 and 251–253 cm^{-1}. If a trans effect operates in these compounds, their scarcity and the complexity of the spectra would make finding an absorption of variable frequency very difficult. The Pt–I stretching frequencies lie below 200 cm^{-1}, outside the capability of our spectrophotometer.

Registry No. $Pt(phen)Cl_2$, 18432-95-6; $Pt(phen)Br_2$, 42847-12-1; $Pt(phen)I_2$, 42847-13-2; $Pt(phen)Cl_4$, 17030-27-2; $Pt(phen)Br_2Cl_2$, 53432-67-0; $Pt(phen)Cl_2Br_2$, 53495-30-0; $Pt(phen)Br_4$, 53432-68-1; $Pt(phen)Cl_2(I_3)_2$, 53432-69-2; $Pt(phen)Br_2I(I_3)$, 53432-55-6; $Pt(phen)I_4$, 53432-56-7; $Pt(phen)I_3(I_3)$, 53432-57-8; $Pt(phen)Br_3Cl$, 53432-58-9; $Pt(phen)Br_2ICl$, 53432-59-0; $Pt(phen)Cl_3I$, 53432-60-3; $Pt(phen)I_3CN$, 53432-61-4; $Pt(phen)Cl_2(SCN)_2$, 53432-62-5; $Pt(phen)Br_2(SCN)_2$, 53466-61-8; $Pt(phen)ICl_3$, 53495-29-7; $Pt(phen)I_3Cl$, 53432-63-6; Cl_2, 7782-50-5; Br_2, 7726-95-6; I_2, 7553-56-2; ICl, 7790-99-0; ICN, 506-78-5; $(SCN)_2$, 505-14-6; NOCl, 2696-92-6.

References and Notes

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(6) In writing the formulas of the compounds, the authors place the ligands that are in the same plane as phenanthroline first followed by the ligands axial to that plane. In the names of the compounds, the ligands are given in the order recommended by the 1957 report of the IUPAC Commission on the Nomenclature of Inorganic Chemistry: *J. Amer. Chem. Soc.*, **82**, 5523 (1960). The designation cis or trans refers to the first two ligands named; thus cis indicates ligands in the plane of phenanthroline and trans indicates axial ligands of normal oxidative addition products.
(7) In order to distinguish the triiodide ligand from three iodide ligands, the authors place the triiodide ligand in parentheses in symbolic formulas and its name in parentheses in compound names.
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Magnetic Exchange in Copper(II) Complexes of 7-Azaindole

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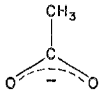
The ligand 7-azaindole (denoted by LH) has been found to form a variety of complexes with divalent copper. These complexes are formulated as $Cu(CH_3CO_2)_2 \cdot LH$, $Cu(CH_3CO_2)(L) \cdot LH$, $Cu(CH_3CO_2)(L) \cdot py$, and $CuL_2 \cdot 2DMSO$. Variable-temperature magnetic susceptibility measurements indicate that substantial pairwise antiferromagnetic exchange between the copper atoms occurs in each case. Various other physical measurements including infrared, electronic, mass, and esr spectroscopy have been employed in the characterization of the complexes. A discussion of the probable molecular structures of the complexes is given. It is proposed that deprotonated 7-azaindole bridges two copper atoms in a syn,syn configuration. The possibility of a superexchange pathway involving triatomic deprotonated 7-azaindole bridges between two copper atoms is also considered.

Introduction

Nonlinear triatomic bidentate groups can function either as simple chelates or as binucleating ligands. The bridging potentialities of carboxylate anions, *e.g.*, acetate (**1**) were originally classified[2] in terms of syn,syn, anti,anti, or anti,syn conformations of OCO, the syn,syn mode being the basis of the binuclear copper(II) acetate structure.[3] The anion of 1,3-diphenyltriazene (**2**) provided the first examples[2,4] of binuclear metal complexes based on the syn,syn bridging by the triatomic NNN group and confirmatory X-ray structural evidence[5] is now available for the $Ni_2(dpt)_4$, $Pd_2(dpt)_4$, and $Cu_2(dpt)_4$ dimers (dpt denotes the 1,3-diphenyltriazenido anion).



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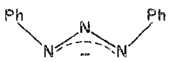

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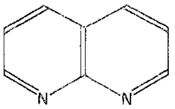

3

An investigation of the bridging potential of the triatomic NCN group represents a natural extension of these investigations. Initially, the neutral 1,8-naphthyridine (3) was studied in the hope that the ligating power of pyridine would enable the isolation of a more extended range of transition metal dimers. In the event, evidence for dimeric cations of the type $[M_2(1,8\text{-naphthyridine})_4]^{4+}$ has not emerged, either from our own studies[6] or from the extensive work of Hendricker[7] with