30. This is greater than that reported by Haake and Turley[3] for Pt(dimeen)$(NH_3)_2^{2+}$, but rather less than values reported for *N*-methylethylenediamines by Buckingham, *et al.*,[4] and Erickson.[5] However, as pointed out by Buckingham, *et al.*,[4] values of the inversion rates and retention ratios obtained by this method could easily be in error (especially in this case where there is a considerable increase in the concentration of NaOH to change the pH from 11.9 to 12.8).

Discussion

Rates of N-Deuteration.—The rate of N-deuteration for the racemic isomer of Pt(dimetn)$(NH_3)_2^{2+}$ is almost twice that for the meso isomer. This can be rationalized if it is assumed that in a six-membered ring an axial proton attached to a N atom which also carries an equatorial methyl group is somewhat shielded from the attack by an hydroxide ion which initiates the exchange. The equatorial methyl group and the axial H atom on the central carbon atom would be chiefly responsible for this steric hindrance. For the meso isomer, both amino protons would be in this sheltered axial orientation in the preferred conformation. For the racemic isomer, both chair conformations are equivalent and each amino proton would spend 50% of its time in the less sheltered equatorial orientation, where attack by OH^- can occur more readily. For five-membered chelate rings, the substituents on the N atoms are rather less decisively "axial" or "equatorial" in character than their counterparts in six-membered (chair) chelate rings, and "axial" amino protons do not appear to be protected from the attack appreciably more than "equatorial" protons. Thus, there appears to be little difference in rates of N-deuteration between the isomers of Pt(dimeen)$(NH_3)_2^{2+}$, and the exchange rate is greater than for the dimetn complexes.[3]

Platinum–Proton Coupling Constants.—Erickson[5] pointed out that the Pt–N bond strength was considerably reduced when the N atom carried two methyl groups (*e.g.*, such bonds could be broken in concentrated KOH solution). This was reflected in low values of $J_{\text{Pt-N-CH}_2\text{-}}$ and $J_{\text{Pt-N-CH}_3}$ compared with complexes of less substituted diamines. A similar effect is observed for $J_{\text{Pt-N-CH}_2\text{-}}$ of Pt(tetrameen)$(NH_3)_2^{2+}$ and Pt (tetrametn)$(NH_3)_2^{2+}$. The values of $J_{\text{Pt-N-CH}_2\text{-}}$ for these complexes (27 and 30 Hz, respectively) are much lower than for the corresponding ethylenediamine (41.5 Hz) and trimethylenediamine (43.0 Hz) complexes.[11] The exact orientations of the methylene protons in the preferred conformations may also have some effect on the coupling constants.[13] The values of $J_{\text{Pt-N-CH}_3}$ for these complexes (33.5 and 32.3 Hz for tetrameen and tetrametn complexes, respectively) are also low compared with the corresponding complexes of dimeen (39.9, 39.2 Hz) and dimetn (meso 36.5 Hz, racemic 38.5 Hz).

If $J_{\text{Pt-N-CH}_3}$ in the isomers of Pt(dimetn)$(NH_3)_2^{2+}$ is governed by the orientation of the *N*-methyl groups in the preferred conformation, then the coupling constant in the meso isomer represents the coupling to an equatorial *N*-methyl group, while the coupling in the racemic isomer will be the average of the couplings to axial and equatorial *N*-methyl groups. This leads to the conclusion that $J_{\text{Pt-N-CH}_3\text{(ax)}}$ is greater than $J_{\text{Pt-N-CH}_3\text{(eq)}}$ by 4 Hz. The comparatively small difference in coupling constants for the isomers of Pt(dimeen)$(NH_3)_2^{2+}$ again probably illustrates the less distinct "axial" and "equatorial" nature of N substituents in five-membered chelate rings.

Acknowledgment.—T. G. A. acknowledges the award of a CSIRO postgraduate studentship.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ARIZONA, TUCSON, ARIZONA 85721

Effect of Basicity of Nonreacting Ligands on the Rate of Reaction of Dithiooxamide with Dichloro(phenanthroline)platinum(II) Derivatives

BY RONALD C. CONRAD AND JOHN V. RUND*

Received April 8, 1971

An examination has been made of the kinetics of the displacement by dithiooxamide (DTOA) of chloride from Pt(phenX)Cl_2 to give [Pt(phenX)(DTOA)]Cl_2 (phenX is one of a series of ten substituted phenanthroline ligands). The reaction is carried out in nitromethane solution at 25° and is followed by conductivity. The displacement of the first chloride is rate determining, and the rate law is of the usual form, rate = k_1[complex] + k_2[complex][entering ligand]. First-order rate constants are small and without apparent pattern. There is a linear free energy relation between the second-order rate constant and the basicity of the phenanthroline, complexes with the least basic phenanthrolines reacting most rapidly. The most reactive complexes are found to have the strongest bonds to the leaving groups. These results are taken to indicate: (1) that the activation energy is expended on making the bond to the incoming nucleophile; (2) that decreasing the basicity of phenanthroline increases the electrophilicity of platinum through σ bonding; (3) the σ-bonding effect is the same whether it operates cis or trans to the leaving group.

In the extensively studied substitution reactions of square-planar complexes, the ligand trans to the leaving group has received the bulk of the attention.[1,2] Its ability to promote substitution is considered to have two aspects, one arising from its σ bonding ability and the other arising from its π bonding ability. The σ trans effect is generally ascribed to a weakening of the bond to the leaving group. Strong σ bonding ligands in the trans position get a large share of the p character

---

(1) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 351.

(2) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1965, p 18.

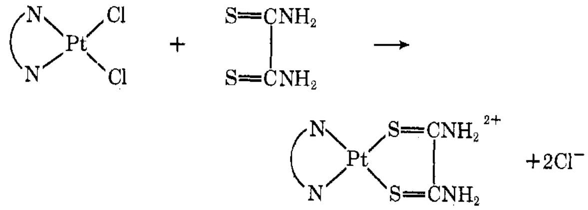
of the metal hybrid orbital, consequently the leaving group must use an orbital with less directional character (more s character). This argument seems reasonable when the attainment of the transition state is mostly a matter of weakening the bond to the leaving group.

Langford and Gray propose that if the entering group is much higher in the trans effect series than the leaving group, then reaching the transition state would involve the formation of a bond to the entering group, rather than the weakening of a bond to the leaving group. Under these circumstances, the σ-trans-effect trend would seem to be reversed. A strong σ bonder in the trans position would push more electron density onto the metal ion and reduce its electrophilicity, thus slowing down the reaction. Reduction in electrophilicity has been considered by Cattalini.[3]

No good test of this hypothesis appears in the literature. Trans-effect research has generally involved changing the atom that was coordinated at the trans position. Such a general change introduces an element of uncertainty about what property of bonding is being altered. A better test would employ a series of trans ligands that bond through the same atom. The hybridization of the coordinated atom and the geometry of the ligand should be kept as constant as possible, and the entering group should lie well above the leaving group in the trans-effect series.

Some results have been published in which the trans ligand but not the trans coordinating atom has been changed. Rates of replacement of chloride by pyridine in *trans*-$Pt(PEt_3)_2LCl$ (where L is one of a series of para-substituted phenyl groups), in *cis*-$Pt(PR_3)_2Cl_2$ (where R is ethyl or *n*-propyl),[4] and in $Au(AA)Cl_2^+$ (where AA is 2,2′-bipyridyl, 1,10-phenanthroline, or 5-nitro-1,10-phenanthroline)[5] have been measured. Pyridine, however, is a poorer trans director than chloride. Evidence has been obtained for olefin exchange in *trans*-$Pt(CH_3CH{=}CHCH_3)LCl_2$ (where L is one of a series of 4-substituted pyridines),[6] but the rates were not measured.

We report the rates of a series of reactions of the type



(1)

where the nitrogen chelate is 2,2′-bipyridyl, 1,10-phenanthroline, or one of a series of substituted phenanthroline molecules. The entering group, dithiooxamide (DTOA), is very high in the trans-effect series. This reaction was originally reported for the bipyridyl complex by Haake.[7] Replacement of the first chloride is rate determining, and ring closure is rapid, leading to a simple rate law.

Substituents that have been placed on the nitrogen chelate preserve the hybridization of nitrogen; they are remote from platinum and should cause no steric effect; and they do not affect the geometry of the chelate, which will be shown to be important in later discussion. The system we have chosen alters the group cis to the leaving group in the same way as it alters the one trans to it. The cis effect is the least systematically studied of all effects in square-planar substitution mechanisms. One series of compounds has been examined in which σ cis effects have been varied[3] and which meets the criteria described above. The results are similar to the ones we obtained. We will argue that the changes we have made principally affect the σ bonding character of the ligand and that the alteration in rate is caused by the change in electrophilicity of platinum. The effect does not appear to have any particular directional character.

Experimental Section

Chemicals.—Potassium tetrachloroplatinate(II) was prepared as described in ref 8 and 9. *Anal.* Calcd for K_2PtCl_4: Cl, 34.16. Found: Cl, 34.13. The preparation and analysis of potassium tetrachloropalladate(II) was given in ref 10. Bipyridyl came from Distillation Products Industries, and the following phenanthroline compounds were purchased from G. Frederick Smith Chemical Co.: the 4,7-dimethyl, 4,7-diphenyl, 5,6-dimethyl, and 3,4,7,8-tetramethyl derivatives. Other phenanthroline derivatives were prepared by published methods, and their identities were confirmed by melting point determinations: 1,10-phenanthroline,[11] 4,7-dichloro-1,10-phenanthroline,[12] 4,7-dibromo-1,10-phenanthroline,[13] and 4,7-dimethoxy-1,10-phenanthroline.[14] 5-Nitro-1,10-phenanthroline and 1,10-phenanthroline-5,6-quinone were prepared by a modification of the method of Smith and Cagle.[15] 1,10-Phenanthroline monohydrate (7.5 g) was dissolved in 40 ml of fuming H_2SO_4. Concentrated HNO_3 (20 ml) was added slowly with stirring. (The original directions called for addition at such a rate that the temperature approached but did not exceed 170°. Our experience was that the mixture refluxed at 90° and did not get hotter.) The reaction flask was fitted with a reflux condenser and heated in a 160–170° oil bath for 0.5 hr. After being cooled to room temperature, the mixture was carefully poured over crushed ice; 30% NaOH (about 150 ml) was added to give a basic litmus test, and then just enough HCl was added to reverse the litmus. The precipitate was filtered out and washed with 500 ml of water. The two filtrates were combined and set aside. The pale yellow solid, 5-nitro-1,10-phenanthroline, was recrystallized from about 2 l. of boiling water with addition of decolorizing charcoal and dried under vacuum. The product weighed 4.0 g (43%) and had mp 200° (lit.[15] 200°). After a day, yellow crystals had appeared in the filtrate mentioned above. These were collected and recrystallized twice from acetone. The product, 1,10-phenanthroline-5,6-quinone, weighed 0.8 g (10%) and had mp 245–248° (lit.[16] 245–248°). *Caution:* work with even minute quantities of this quinone causes severe sneezing and nasal irritation.

Dichloro(phenanthroline)platinum(II) and its derivatives were all prepared by the same general method. Care was taken to prevent introduction of dust and other insoluble impurities, since contaminants were not easily removed owing to insolubility of the product. Filtered, deionized water (2 l.) was heated to boiling on a stirring hotplate. K_2PtCl_4 (0.415 g, 1 mmol) was added, followed immediately by 1 mmol of the phenanthroline derivative which had been dissolved in a minimum quantity of 1 *N* HCl and filtered if necessary. Boiling and stirring were maintained for 4 hr, and water was added as needed. The yellow product slowly precipitated and was collected by filtration from the hot solution.

---

(3) L. Cattalini, G. Marangoni, and A. Cassol, *Inorg. Chim. Acta*, **3**, 74 (1969).

(4) F. Basolo, J. Chatt, H. B. Gray, R. G. Pearson, and B. L. Shaw, *J. Chem. Soc.*, 2207 (1961).

(5) L. Cattalini, A. Doni, and A. Orio, *Inorg. Chem.*, **6**, 280 (1967).

(6) P. D. Kaplan, P. Schmidt, A. Brause, and M. Orchin, *J. Amer. Chem. Soc.*, **91**, 85 (1969).

(7) P. Haake and P. A. Cronin, *Inorg. Chem.*, **2**, 879 (1963).

(8) R. N. Keller, *Inorg. Syn.*, **2**, 247 (1946).

(9) G. B. Kauffman and L. A. Teter, *ibid.*, **7**, 232 (1963).

(10) J. V. Rund, *Inorg. Chem.*, **9**, 1211 (1970).

(11) K. Madeja, *J. Prakt. Chem.*, **17**, 104 (1962).

(12) H. R. Snyder and E. H. Frier, *J. Amer. Chem. Soc.*, **68**, 1320 (1946).

(13) F. H. Case, *J. Org. Chem.*, **16**, 941 (1951).

(14) J. V. Rund and K. G. Claus, *J. Amer. Chem. Soc.*, **89**, 2256 (1967).

(15) G. F. Smith and F. W. Cagle, *J. Org. Chem.*, **12**, 781 (1947).

(16) R. D. Gillard, R. E. Hill, and R. Maskill, *J. Chem. Soc. A*, 1447 (1970).

TABLE I

ANALYTICAL DATA

Compound	Formula	C, %		H, %		Cl, %	
		Calcd	Found	Calcd	Found	Calcd	Found
[Pt(4,7-dimethoxy-1,10-phenanthroline)Cl$_2$]	$C_{14}H_{12}Cl_2N_2O_2Pt$	33.2	32.5	2.38	2.65	14.1	13.6
[Pt(3,4,7,8-tetramethyl-1,10-phenanthroline)Cl$_2$]	$C_{16}H_{16}Cl_2N_2Pt$	38.2	38.1	3.22	3.49	14.1	13.9
[Pt(4,7-dimethyl-1,10-phenanthroline)Cl$_2$]	$C_{14}H_{12}Cl_2N_2Pt$	35.5	35.6	2.53	2.80	15.0	15.0
[Pt(5,6-dimethyl-1,10-phenanthroline)Cl$_2$]	$C_{14}H_{12}Cl_2N_2Pt$	35.5	36.0	2.53	2.74	15.0	14.8
[Pt(1,10-phenanthroline)Cl$_2$]	$C_{12}H_8Cl_2N_2Pt$	32.3	32.4	1.80	1.93	15.9	15.8
[Pt(4,7-diphenyl-1,10-phenanthroline)Cl$_2$]	$C_{24}H_{16}Cl_2N_2Pt$	48.2	48.1	2.67	2.67	...	...
[Pt(2,2′-bipyridyl)Cl$_2$]	$C_{10}H_8Cl_2N_2Pt$	28.5	28.5	1.90	2.09	16.6	16.9
[Pt(5-nitro-1,10-phenanthroline)Cl$_2$]	$C_{12}H_7Cl_2N_3O_2Pt$	29.4	29.3	1.44	1.49	14.4	14.3
[Pt(4,7-dibromo-1,10-phenanthroline)Cl$_2$]	$C_{12}H_6Br_2Cl_2N_2Pt$	23.9	24.4	0.99	1.30	11.8	11.7
[Pt(4,7-dichloro-1,10-phenanthroline)Cl$_2$]	$C_{12}H_6Cl_4N_2Pt$	28.0	28.1	1.77	1.52	27.6	27.6
[Pt(1,10-phenanthroline-5,6-quinone)Cl$_2$]	$C_{12}H_6Cl_2N_2O_2Pt$	30.3	30.0	1.26	1.40	14.9	14.9
[Pd(1,10-phenanthroline)Cl$_2$]	$C_{12}H_8Cl_2N_2Pd$	40.3	40.3	2.23	2.39	...	...
[Au(1,10-phenanthroline)Cl·H$_2$O	$C_{12}H_{10}AuCl_3N_2O$	28.7	28.9	2.00	2.03	21.3	21.7

After being boiled in 6 *N* HCl with stirring for another 4 hr, it was filtered out, washed with water, and dried in a vacuum desiccator. Pt(bipy)Cl$_2$ was prepared by a method analogous to that given for Pt(phen)Cl$_2$ in ref 17. Pd(phen)Cl$_2$ was prepared as described (Livingstone[18]) and recrystallized from nitrobenzene at 150°. Au(phen)Cl$_3$ was obtained as the monohydrate by the method of Harris.[19] Loss of weight after heating for 24 hr at 100° was in reasonable agreement with removal of 1 mol of water.

The entering nucleophile, dithiooxamide, $H_2NC(S)C(S)NH_2$, was purchased from the J. T. Baker Chemical Co. and recrystallized twice from ethanol. The solvent for the reaction, nitromethane, was from Matheson, Coleman, and Bell. It was distilled through a 30-cm Vigreux column and stored over 4A Molecular Sieves.

Kinetics.—The reaction between Pt(phen)Cl$_2$ (and derivatives) and DTOA was carried out in nitromethane solution at 25.0°. Its progress was monitored by conductivity, using a pair of bright platinum electrodes sealed into the reaction flask. Measurements were made with an Industrial Instruments Model RC 16B2 conductivity bridge. DTOA concentration was larger enough than that of the complex to give pseudo-first-order kinetics. The observed rate constant, k_{obsd}, was obtained from the slope of a graph of ln ($C_\infty - C_0 - C_t$) *vs.* time, where C_0 and C_∞ are the conductivities at the beginning and end of the reaction, and C_t is the increase in conductivity at time *t*. Reactions were followed for at least one half-life and exhibited good first-order kinetics. Figure 1 shows a sample kinetic run. Two to four reactions were run for each set of conditions to obtain the observed rate constant. Five different concentrations of DTOA were used for each complex. The rate law was of the usual form[20] for platinum(II) substitution reactions

$$\text{rate} = k_1[\text{complex}] + k_2[\text{complex}][\text{entering ligand}]$$

In some cases, however, k_1 was as small as or smaller than the standared deviation in k_{obsd} and so could not be assigned a value significantly different from zero.

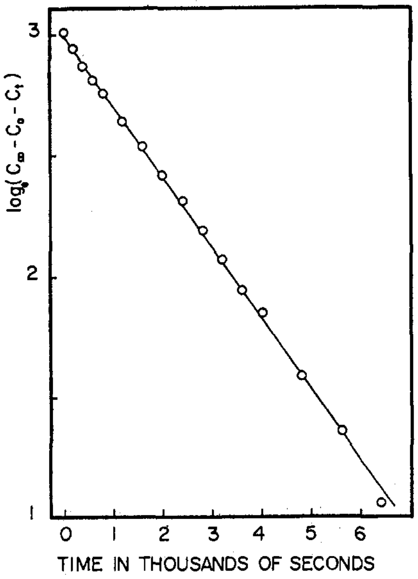


Figure 1.—Sample kinetic plot. [DTOA] = 35.5 × 10^{-4} *M*, [dichloro(4,7-dichloro-1,10-phenanthroline)platinum(II)] = 4.77 × 10^{-5} *M*.

In determining kinetics by conductivity, the problem of ion pairing must be considered. The reactants in our study are nonelectrolytes, and conductivity increases as the reaction proceeds, owing to ionization of the product. If association occurs among product ions, then the first-order rate constant of the reaction will appear to decrease with time, causing nonlinearity in kinetic plots. In the extreme case, where most of the product exists as a neutral ion pair, the reaction will appear to be second order. We take the absence of an upward curvature in graphs such as Figure 1 to indicate that ion pairing is not occurring to a significant extent in nitromethane at the concentrations we have used.

Spectra.—Infrared spectra of the complexes in KBr discs were measured on a Beckman IR 12 spectrophotometer between 400 and 300 cm^{-1}. Assignment of Pt–Cl symmetric and asymmetric stretching frequencies was based on those for Pt(bipy)Cl$_2$.[21] Ultraviolet spectra of phenanthroline molecules in methanol solutions were recorded on a Cary 12 spectrophotometer between 350 and 280 nm. Absorption frequencies were obtained using a Du Pont 310 curve resolver. Assignment of the lowest $\pi \rightarrow \pi^*$ transition was based on the dependence of the transition energy on solvent polarity. The absorption labeled $n \rightarrow \pi^*$ in Table III was the only one which disappeared when an aqueous solution of phenanthroline was acidified, indicating the involvement of the unshared electron pairs on the nitrogens.[22]

pK_a's.—The basicities of most phenanthrolines used in this research had been determined. Using the method of Schilt and Smith,[23] we made measurements on the 5,6-quinone and the 5,6-dimethyl derivative. The pK_a of the former had not been reported. The latter has a published pK_a that appears to be unreasonable. Methyl substitution at any carbon should increase the pK_a, but our previous measurement[24] had shown a decrease. A repetition of the determination after careful purification of the compound gave a considerably different result. Since the 5,6-dimethyl-1,10-phenanthroline used in ref 24 gave both an incorrect pK_a and anomalous kinetics results, the purity of the compound must be suspect.

Results

Analytical data for the complexes are given in Table I. The platinum compounds containing derivatives of 1,10-phenanthroline have not previously been reported.

With excess DTOA, Pt(phen)Cl$_2$ complexes reacted by a first-order process, observed rate constants of

---

[17] F. A. Palocsay and J. V. Rund, *Inorg. Chem.*, **8**, 542 (1969).

[18] S. E. Livingstone, *J. Proc. Roy. Soc. N. S. W.*, **85**, 1511 (1951).

[19] C. M. Harris, *J. Chem. Soc.*, 682 (1959).

[20] Reference 1, p 377.

[21] T. Boschi, G. Deganello, and G. Carthuran, *J. Inorg. Nucl. Chem.*, **31**, 2423 (1969).

[22] J. G. Calvert and J. N. Pitts, "Photochemistry," New York, N. Y., 1966, pp 260–262.

[23] A. A. Schilt and G. F. Smith, *J. Phys. Chem.*, **60**, 1546 (1956).

[24] J. V. Rund and K. G. Claus, *Inorg. Chem.*, **7**, 860 (1968).

TABLE II

OBSERVED RATE CONSTANTS[a] FOR REACTION 1

$Pt(AA)Cl_2$ AA[b]	[DTOA[c]], $M \times 10^4$				
	7.10	14.20	21.30	28.40	35.50
4,7-diOMe	1.7 ± 0.07	3.0 ± 0.2	3.7 ± 0.2	4.7 ± 0.2	5.6 ± 0.01
3,4,7,8-tetraMe	3.3 ± 0.2	4.9 ± 0.3	6.5 ± 0.0	9.3 ± 0.3	10.8 ± 0.2
4,7-diMe	3.1 ± 0.5	4.6 ± 0.0	7.1 ± 0.1	9.6 ± 0.2	12.1 ± 0.4
5,6-diMe	5.2 ± 0.4	7.8 ± 0.6	11.6 ± 0.7	14.7 ± 0.4	17.6 ± 0.6
phen	3.2 ± 0.1	7.5 ± 0.3	10.5 ± 0.7	13.3 ± 0.6	17.9 ± 0.4
4,7-diPh	5.3 ± 0.07	9.7 ± 0.08	14.3 ± 0.07	18.6 ± 0.2	22.0 ± 0.5
bipy	5.5 ± 0.03	10.2 ± 0.6	15.8 ± 0.4	21.5 ± 0.6	26.5 ± 1.1
5-NO_2	6.1 ± 0.2	12.0 ± 0.1	16.8 ± 1.6	23.3 ± 0.3	28.3 ± 0.1
4,7-diBr	8.6 ± 0.4	14.0 ± 0.5	21.8 ± 2.6	24.8 ± 1.0	31.3 ± 0.5
4,7-diCl	5.7 ± 0.03	10.9 ± 0.6	15.1 ± 0.0	23.6 ± 0.3	29.0 ± 0.9
5,6-quin	11.1 ± 0.2	20.8 ± 1.3	30.7 ± 1.0	39.2 ± 2.2	

[a] $k_{obsd} \times 10^5$ sec^{-1}. [b] For fuller description of the ligand, see Table I, in which the compounds are listed in the same order. [c] DTOA = dithiooxamide.

TABLE III

REACTION CONSTANTS FOR REACTION 1 AND OTHER PHYSICAL PROPERTIES OF $Pt(AA)Cl_2$ COMPLEXES

$Pt(AA)Cl_2$ AA[a]	$k_1 \times 10^5$, sec^{-1}	$k_2 \times 10^2$, M^{-1} sec^{-1}	Log k_2	pK_a[b]	ν(Pt–Cl), cm^{-1}	$\lambda(n \rightarrow \pi^*)$, nm	$\lambda(\pi \rightarrow \pi^*)$, nm
4,7-diOMe	0.9	1.34	0.127	6.45[c]	336	336.5	308.5
3,4,7,8-tetraMe	0.7	2.88	0.459	6.31[c]	343,336	329	306
4,7-diMe	0.3	3.27	0.515	5.97[d]	339	325.5	300.5
5,6-diMe	1.7	4.55	0.658	5.20[e]	354,341	334	305
phen	~0	4.92	0.691	4.96[f]	356,342	323.5	309.5
4,7-diPh	1.3	5.94	0.771	4.84[c]	345,338	333	305
bipy	~0	7.50	0.875	4.30[g]	348,338	...	...
5-NO_2	0.6	7.83	0.893	3.57[h]	348	326	313
4,7-diBr	3.1	8.00	0.903	~3.0[i]	352,341	331.5	304.5
4,7-diCl	~0	8.40	0.924	3.03[c]	346	330	302
5,6-quin	2.0	13.1	1.117	3.14[e]	354,346	...	303.5

[a] See Table I for more complete identification. [b] Refers to the equilibrium $BH^+ = B + H^+$. [c] Reference 23. [d] Reference 24. [e] Present work. [f] C. H. Cook and F. A. Long, *J. Amer. Chem. Soc.*, **73**, 4119 (1951). [g] J. H. Balendale and P. George, *Trans. Faraday Soc.*, **46**, 55 (1950). [h] W. W. Brandt and D. K. Gullstrom, *J. Amer. Chem. Soc.*, **74**, 3532 (1952). [i] Estimated using Hammett substituent parameters.

which are listed in Table II. The reaction of the palladium complex was too fast to follow by conductivity, but the overall conductivity change was the same as for platinum. The gold complex also reacted rapidly, but the product precipitated before the reaction was complete, so the final conductivity could not be compared with those of other reactions. Platinum rate constants were linear functions of DTOA concentrations. Some sample graphs of k_{obsd} *vs.* [DTOA] are shown in Figure 2. Rate constants, k_1 and k_2, derived from the intercepts and slopes of these graphs, are listed in Table III.

The first-order rate constants show no recognizable pattern. They are usually associated with the rate at which the solvent displaces the leaving group from the complex. In order to confirm this, we made a direct measurement of the solvolysis rate constant for the 5-nitro-1,10-phenanthroline complex. It was 0.3×10^{-5} sec^{-1}, compared with 0.6×10^{-5} sec^{-1} for the indirect measurement. The agreement is reasonable, considering the size of the standard deviations of k_{obsd}.

The trend in the second-order rate constant, k_2, is well correlated with the change in basicity of phenanthroline (see pK_a's in Table III). Complexes with less basic phenanthrolines gave faster reactions. A weak but probably significant correlation exists between rate and platinum–chlorine stretching frequency. Because the same atoms and geometries are being compared, the frequency of vibration give some indication of the relative bond strengths. If the trend is real, then the strongest bonds to the leaving groups occur in complexes that react most rapidly.

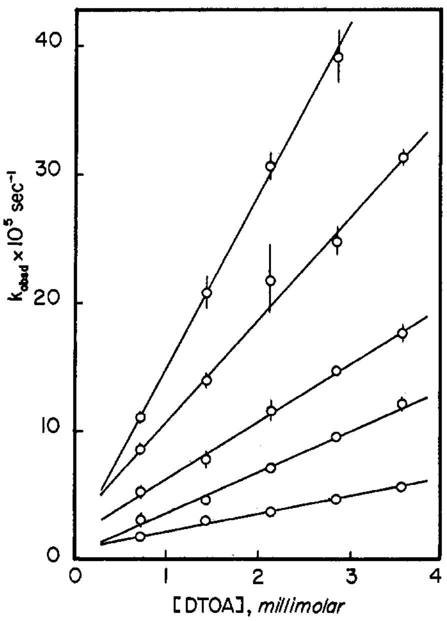


Figure 2.—Observed rate constants as functions of [DTOA]. In descending order, lines refer to reactions of the following dichloro(phenanthroline)-platinum(II) compounds: the 5,6-quinone, the 4,7-dibromo derivative, the unsubstituted compound, the 4,7-dimethyl derivative and, the 4,7-dimethoxy derivative.

No relation is apparent between the rates and either of the absorption energies in the ultraviolet spectra of the phenanthroline molecules. The two absorptions that were chosen for examination were the n → π^*

transition involving the nonbonding electron pairs on the nitrogens and the lowest-energy $\pi \rightarrow \pi^*$ transition. Our attempt has been to change the rates without changing the π influence of the trans ligand, so the absence of a rate correlation is as expected.

Conclusions

Reactivity of Pt(phen)Cl_2 compounds generally increases with decreasing basicity of phenanthroline. The linear free energy plot of log k_2 *vs.* pK_a (Figure 3) shows this trend clearly, although not all points lie on a straight line. A good fit would indicate that the substituents are affecting only the σ bonding character of the ligand. In fact, some are causing small changes in the π bonding as well. The π donors, chloride, bromide, and methoxide, are the substituents with points lying below the line; they contribute electron density to the π orbitals of the phenanthroline and interfere with a similar contribution by the platinum. (Although we have no explanation for the position of the 5-nitro compound below the line, note that it is the only unsymmetrical phenanthroline, which complicates considerations of its reactivity.) Had it been possible to keep the π contributions to the trans labilization invariant, the activation energy could be expected to be well correlated with the basicity of phenanthroline.

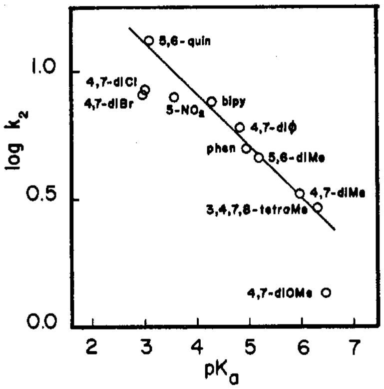


Figure 3.—Linear free energy relation between the second-order rate constant of reaction 1 and the basicity of the phenanthroline derivative.

Our infrared data suggest that the most basic ligands weaken the bond to the leaving group. This is consistent with the usual prediction of the trans effect, and a similar result has been obtained for the series Pt(en)$_2$$Cl_2$, *cis*-Pt(py)$_2$$Cl_2$, and Pt(bipy)$Cl_2$[21] (see Table IV). The fact that the bipyridyl compound, which had the strongest Pt–Cl bond, reacted most rapidly was rationalized by postulating a resonance stabilization that developed as the reaction coordinate was traversed.[21] Stabilization depended on the existence of an aromatic ring that contained the platinum atom. We would offer a somewhat more conventional explanation: the bipyridyl complex is labilized by the π-trans effect, whereas pyridine and ethylenediamine complexes are not. Molecular models show that neither of the pyridines in *cis*-Pt(py)$_2$$Cl_2$ is likely to be capable of being coplanar with the coordination plane of platinum, so that pyridine pπ orbitals will not be in position to withdraw electron density from platinum d_{xz} or d_{yz} orbitals. Bipyridyl, on the other hand, is fixed in the coordination plane of platinum. This possibility was first suggested by Haake.[7] Trans labilization is very sensitive to π interactions, and, as shown above, in order to argue with some certainty about the σ trans effect, one must fix not only the identity and hybridization of the coordinating atom but also the geometry of the ligand. Explaining the relation between our infrared and rate data presents no problem. Since bond making dominates the activation energy, small changes in the strength of the bond to the leaving group should have no effect on the rate.

TABLE IV
RATE CONSTANTS AND Pt–Cl STRETCHING FREQUENCIES FOR SOME PLATINUM COMPLEXES

Compound[a]	$k_1 \times 10^5$, sec^{-1}	$k_2 \times 10^2$, $M\ sec^{-1}$	ν(Pt–Cl), cm^{-1}
Pt(en)$_2$$Cl_2$	1.9[b]	0.4[b]	334, 315[c]
cis-Pt(py)$_2$$Cl_2$	~0	0.4	343, 329
Pt(bipy)Cl_2	~0	34	351, 358

[a] en = ethylenediamine, py = pyridine, bipy = bipyridyl.
[b] Data from ref 7, for reaction with DTOA at 25° in methanol.
[c] Data from ref 21.

We find faster rates associated with stronger bonds to the leaving group, so approach to the transition state may reasonably be supposed to involve formation of a bond to the entering group, since the electrophilicity of the platinum atom determines the strength of both bonds. In this system, electrophilicity is being varied by changing the basicity of the phenanthroline ligand. The relation between rates and basicities is inconsistent with the usual prediction of the σ trans effect and shows the importance of considering whether the activation energy for the overall reaction is involved with formation or dissociation of the five-coordinate intermediate. When π bonding effects are constant, stronger σ bonding ligands in nonreacting coordination positions hinder formation of the bond to the entering group and assist in weakening the bond to the leaving group.

Cattalini[3] has examined the kinetics of replacement of chloride by iodide and thiocyanate in a series of complexes, *trans*-Pt(pyX)$_2$$Cl_2$, where pyX is one of three substituted pyridine ligands. The results are very similar to ours: an increase in the K_a of the pyridine by a factor of 10^4 is accompanied by a tenfold decrease in rate. The changes in basicity in this system were made in ligands cis to the leaving group, whereas in our system, one ligand was cis and the other was trans. To conclude that in our reaction the cis effect outweighs the trans effect would be logical, but it is more reasonable to suppose that the effects are complementary, which is to say insensitive to the position of the nonreacting ligand. The conclusion that seems best to fit the presently available data on reactions in which only bond making is important is the following: if a group that is high in the trans-effect series displaces a group low in the series from a platinum(II) complex and if the changes in the nonreacting ligands are entirely confined to changes in basicity, then the complex with the least basic nonreacting ligands (irrespective of their positions, so long as the position are unchanged) will react most rapidly.

Acknowledgment.—This investigation was supported by Biomedical Sciences Support Grant FR 07002 from the General Research Support Branch, Division of Research Resources, Bureau of Health Professions Education and Manpower Training, National Institutes of Health. Dr. Conrad was supported by a National Science Foundation grant which the authors gratefully acknowledge.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
QUEEN'S UNIVERSITY, KINGSTON, ONTARIO, CANADA

Electron-Spin Delocalization in Antiferromagnetic Dimeric Copper(II) Benzoates

BY R. A. ZELONKA AND M. C. BAIRD*

Received April 2, 1971

The copper(II) salts of benzoic acid, *o*-, *m*-, and *p*-methylbenzoic acid, and 2,6-dimethyl- and 3,5-dimethylbenzoic acid exist as dimers with reduced magnetic moments in acetone solution at room temperature. The solution nmr spectra of these compounds, as well as of $[Cu(formate)_2\cdot urea]_2$ and $[Cu(acetate)_2\cdot urea]_2$, exhibit quite large contact shifts of the proton resonances, consistent with a superexchange mechanism for the spin exchange. The pattern of signs of the contact shifts suggests that spin delocalization from the copper ions is into the σ bonding system of the carboxylate groups, although finite spin densities also appear in the π systems of the aromatic rings, possibly *via* hyperconjugation.

Introduction

The anomalously low magnetic moments of many copper(II) alkanoates have generated considerable controversy for many years. Dimeric compounds of the type $[Cu(RCO_2)_2\cdot L]_2$ (R = alkyl, aryl; L = a neutral or anionic ligand) have been studied most intensively.[1] They have the structure shown in Figure 1, the copper-copper distance being only about 2.64 Å, and are antiferromagnetic with a singlet ground state and a thermally populated triplet excited state.[1]

Although Forster and Ballhausen concluded from molecular orbital considerations that the primary antiferromagnetic interaction is a σ bond formed by the copper $3d_{z^2}$ electrons,[2] opinion in general favors the presence of a δ bond brought about by overlap of the $3d_{x^2-y^2}$ orbitals.[3,4] A number of modifications to these theoretical approaches have been made and have been summarized by Jotham and Kettle,[5] who treated the two copper atoms as a two-hole diatomic molecule while including crystalline field and electron-repulsion effects. Generally these procedures assume a direct copper–copper interaction, although indirect coupling or superexchange mechanisms *via* the bridging carboxylate ligands have also been suggested.[6-8] Very serious doubt concerning the importance of direct copper–copper bonding has been aroused, however, by magnetic and structural studies on the analogous copper(II) formate and acetate dimers $(Me_4N)_2[Cu(RCO_2)_2(NCS)]_2$.[9] Although the acetate has the shorter copper–copper distance, it is the formate which exhibits the greater degree of spin exchange. Since direct metal–metal bonding should increase with shorter bonding distances, it seems likely that the carboxylate bridges play a major role in the spin-exchange interaction.

The present investigation was undertaken in order to gain an insight into the nature and extent of electron delocalization into the carboxylate ligands. It is well-known[10] that delocalization of unpaired electron spin density from a paramagnetic transition metal ion into the molecular orbitals of coordinated ligands can cause quite large contact shifts in the proton nmr spectra of the ligands. In some cases, the magnitude and direction of the contact shifts have given useful information concerning the mode of delocalization of electron density into the ligands, and it was expected that a proton nmr study of a series of dimeric substituted copper(II) benzoates could be very informative in this respect.

Although the relatively long electronic relaxation times of monomeric tetragonal copper(II) complexes[11] generally cause extreme broadening of the nmr spectra of copper complexes, it was hoped that the electron-spin exchange of the dimeric complexes would provide a sufficiently efficient mechanism for electron-spin relaxation that the proton nmr spectrum could be resolved. Previously, Kawamori[12] and Inoue and Kubo[13] have reported variable temperature broad line studies on copper(II) acetate hydrate and two modifications of copper(II) formate, respectively. The latter paper is very pertinent to this work. Large contact shifts of the formate protons were detected and electron delocalization mechanisms were discussed.

Experimental Section

Chemicals.—Benzoic acid and the substituted benzoic acids were purchased from K and K, Inc.; copper sulfate and zinc nitrate from Fisher Scientific Co.

Preparations.—The dimeric copper(II) benzoate derivatives were prepared by the method outlined by Lewis, *et al.*[14] A solution of the relevant acid was prepared in water and the pH was

---

[1] M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, **64**, 99 (1964).

[2] L. S. Forster and C. J. Ballhausen, *Acta Chem. Scand.*, **16**, 1385 (1962).

[3] I. G. Ross and J. Yates, *Trans. Faraday Soc.*, **55**, 1064 (1959).

[4] E. A. Boudreaux, *Inorg. Chem.*, **3**, 506 (1964).

[5] R. W. Jotham and S. F. A. Kettle, *ibid.*, **9**, 1390 (1970).

[6] W. E. Hatfield and J. S. Paschal, *J. Amer. Chem. Soc.*, **86**, 3888 (1964).

[7] A. W. Schlueter, R. A. Jacobson, and R. E. Rundle, *Inorg. Chem.*, **5**, 277 (1966).

[8] G. F. Kokoszka, M. Linzer, and G. Gordon, *ibid.*, **7**, 1730 (1968).

[9] D. M. L. Goodgame, N. J. Hill, D. F. Marsham, A. C. Skapski, M. L. Smart, and P. G. H. Troughton, *Chem. Commun.*, 629 (1969).

[10] D. R. Eaton and W. D. Phillips, *Advan. Magn. Resonance*, **1**, 103 (1965).

[11] B. R. McGarvey, *Transition Metal Chem.*, **3**, 90 (1966).

[12] A. Kawamori, *J. Phys. Soc. Jap.*, **21**, 1096 (1966).

[13] M. Inoue and M. Kubo, *Inorg. Chem.*, **9**, 2310 (1970).

[14] J. Lewis, Y. C. Lin, L. K. Royston, and R. C. Thompson, *J. Chem. Soc.*, 6464 (1965).