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Complexes with *p*-Bromo-N,N-dimethylaniline N-Oxide

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A series of complexes has been prepared with the tertiary amine oxide, *p*-bromo-N,N-dimethylaniline N-oxide. The complexes have the following stoichiometries: $Ca(ClO_4)_2 \cdot 4L$, $Zn(ClO_4)_2 \cdot 4L$, $Mg(ClO_4)_2 \cdot 4L \cdot H_2O$, $Cd(NO_3)_2 \cdot 4L \cdot H_2O$, $Mg(NO_3)_2 \cdot 3L \cdot 2H_2O$, $Pb(NO_3)_2 \cdot 3L \cdot H_2O$, $Ni(NO_3)_2 \cdot 3L \cdot 2H_2O$, $ZnCl_2 \cdot 2L$, and $NiCl_2 \cdot L \cdot H_2O$, where L represents the ligand. Table I shows the analytical data for the complexes. These are the first complexes prepared with a tertiary aniline N-oxide.

Recently, there has been a good deal of interest in complexes prepared with various derivatives of pyridine N-oxide. The bonding in the complexes is through oxygen. The N–O bond exhibits double-bond character in the pyridine N-oxides,[1] whereas the ligand *p*-bromodimethylaniline N-oxide differs from the pyridine N-oxides in that the nitrogen is quaternary and the N–O bond has no double-bond character. Complexes have been prepared with the amine oxide, trimethylamine N-oxide,[2–5] and with the bidentate ligand N,N-dimethylethylenediamine N-oxide.[6] The N-oxide nitrogen is quaternary in both of these ligands. The ligand *p*-bromodimethylaniline N-oxide exhibits steric interaction with the complexes formed. This is also true of the trimethylamine N-oxide, and this steric interaction prevents the metal ions from achieving maximum coordination through the ligand alone. Because of this, less strongly coordinating ligands such as Cl^- enter the coordination sphere as in $ZnCl_2 \cdot 2L$. The maximum coordination number of monodentate tertiary amine N-oxides to a metal ion has been four, with the exception of the chromium perchlorate complex which coordinates to six trimethylamine N-oxide ligands.[5]

With the ligand *p*-bromodimethylaniline N-oxide, the most stable complexes formed with nontransition metal ions. Transition metal complexes can be formed but with the exception of the $NiCl_2$ and $Ni(NO_3)_2$ complexes, decomposition usually takes place within a few hours. The decomposition product shows the presence of *p*-bromodimethylaniline as well as the *p*-bromodimethylaniline N-oxide and tar.

The visible spectrum of the $NiCl_2$ complex was obtained only as a mull owing to its insolubility. The spectrum showed peaks at 412, 652, and 710 mμ with a shoulder at 615 mμ. The spectrum of the $Ni(NO_3)_2$ complex was measured in nitromethane. Absorption peaks appeared at 405 and 650 mμ with ϵ 14 l. mole^{-1} cm^{-1} at 405 mμ.

Table I shows the conductance data for the complexes with *p*-bromodimethylaniline N-oxide. All of the values are in the range expected for 2:1 electrolytes except for the very low value for $ZnCl_2 \cdot 2L$. The low value for the molar conductivity of the zinc chloride complex indicates a nonelectrolyte. In this case, the chloride ions are in the coordination sphere of zinc giving a normal four-coordinate complex.

TABLE I

ANALYTICAL DATA, CONDUCTANCE DATA, AND INFRARED SPECTRAL DATA FOR COMPLEXES

	Elemental analyses, %							Conductance data in nitromethane		
	Carbon		Hydrogen		Nitrogen					
Compound	Calcd	Found	Calcd	Found	Calcd	Found	Mp, °C	Concn, $M \times 10^4$	Λ(molar), cm^2 mho mole^{-1}	Infrared spectra ν(N–O), cm^{-1}
$Ca(ClO_4)_2 \cdot 4L$	35.21	34.84	3.94	3.65	4.76	5.08	120–129 dec	3.80	179	985, 939
$Zn(ClO_4)_2 \cdot 4L$	34.41	34.06	3.61	3.57	4.81	4.96	134–136 dec	9.46	163	970, 943
$Mg(ClO_4)_2 \cdot 4L \cdot H_2O$	34.97	34.77	4.21	3.83	5.16	5.07	109–111	4.24	200	973, 958
$Ca(NO_3)_2 \cdot 4L \cdot H_2O$	34.52	34.36	3.80	3.78	7.29	7.51	113–118	1.04	130	966
$Mg(NO_3)_2 \cdot 3L \cdot 2H_2O$	34.53	34.64	4.17	4.12	7.97	8.41	124–127 dec	6.19	129	968
$Pb(NO_3)_2 \cdot 3L \cdot H_2O$	29.50	28.91	3.25	3.23	6.80	7.01	115–119	Insoluble	. . .	961
$Ni(NO_3)_2 \cdot 3L \cdot 2H_2O$	33.35	33.25	4.07	3.95	7.79	8.08	123–127	9.46	183	965
$ZnCl_2 \cdot 2L$	33.70	33.81	3.74	3.55	5.02	4.93	115–119	21.9	13.9	972, 948
$NiCl_2 \cdot L \cdot H_2O$	26.40	26.42	3.98	3.33	3.65	3.85	96–99	Insoluble	. . .	984, 957
Ligand										962, 941

The N–O stretching frequency in the infrared region (Table I) for the aliphatic amine oxides shows little or no shift on complexation. Gallais[7] has attributed one of the two bands in the 950–970-cm^{-1} region in the spectrum of N,N-dimethylaniline N-oxide to the N–O stretching mode. Kida[3] has calculated a value for the N–O stretching frequency for trimethylamine N-oxide of 960 cm^{-1} and found a value of 950 cm^{-1}. Essentially no shift of the N–O frequency was found upon coordination of trimethylamine N-oxide,[3] and we have observed these same results for *p*-bromodimethylaniline N-oxide. This is anomalous when compared to the complexes of pyridine N-oxide where the N–O frequency decreases as the double-bond character of the

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[1] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1964, p 308.

[2] K. Issleib and A. Kreibich, *Z. Anorg. Allgem. Chem.*, **313**, 338 (1961).

[3] S. Kida, *Bull. Chem. Soc. Japan*, **36**, 712 (1963).

[4] R. L. Carlin and M. J. Baker, *J. Chem. Soc.*, 5008 (1964).

[5] R. S. Drago, J. T. Donoghue, and D. W. Herlocker, *Inorg. Chem.*, **4**, 836 (1965).

[6] J. V. Quagliano and J. T. Summers, *ibid.*, **3**, 1767 (1964).

[7] R. Mathis, R. Wolf, and F. Gallais, *Compt. Rend.*, **242**, 1873 (1956).

N–O bond decreases upon coordination. The fact that the N–O frequency of the aliphatic amine N-oxides shows little or no shift on coordination can be attributed to the single-bond character of the N–O bond. Coordination relieves the electron density around the oxygen but has little effect on the N–O bond.

Experimental Section

Preparation.—The ligand *p*-bromodimethylaniline N-oxide was prepared by oxidizing *p*-bromodimethylaniline with hydrogen peroxide and acetic acid. The complexes were prepared by adding an acetone solution of the ligand to an acetone–dimethoxypropane solution of the metal salt. The complexes usually formed when stirred for several minutes.

Physical Measurements.—The infrared spectra were taken as Nujol mulls on a Beckman IR5A recording spectrophotometer with NaCl optics. The visible spectra were obtained with a Cary Model 14 recording spectrophotometer. Conductance data were obtained using a conductance bridge manufactured by Industrial Instruments Inc. The decomposition products were studied with the aid of thin layer chromatography.

Analyses.—Carbon, hydrogen, and nitrogen analyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Mülheim, West Germany.

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Correspondence

Stereochemically Nonrigid Organometallic Compounds. VI. Configurational Equilibria of π-$C_5H_5Mo(CO)_2$ Allyl Complexes

Sir:

Recently evidence has been presented[1,2] that the temperature dependence of the nmr spectra and their eventual collapse to dynamic A_4X spectra of certain π-allyl complexes is due to a rapid exchange between a π-bonded group and a short-lived σ-bonded intermediate. In certain isoleptic π-allyl complexes, such as $Zr(\pi\text{-}C_3H_5)_4$ and $Pd(\pi\text{-}C_3H_5)_2$, Becconsall, *et al.*,[3] and Wilke, *et al.*,[4] have rationalized the temperature-dependent spectra as resulting from internal rotation of the CH_2 protons about the C–C bond which leads to an averaging of the *syn* and *anti* protons to give A_4X spectra. The former authors rejected a σ–π interconversion on their misinterpretation[3b] of their incompletely averaged high-temperature spectrum of $Pd(\pi\text{-}C_3H_5)_2$. It has been pointed out that other mechanisms can lead to temperature-dependent spectra for π-allyl ligands: either rotation of the π-allyl about an axis through the C–C–C plane[1] or a mechanism involving a flip through a planar intermediate.[5] The former mechanism does not interconvert the *syn* and *anti* protons of the allyl ligand, is clearly operative in the case of $Rh(\pi\text{-}C_3H_5)_3$, and is very probable in the case of $Pd(\pi\text{-}C_3H_5)_2$ although the data cited are insufficient.[3] King[6] has claimed that the existence of four infrared carbonyl stretching frequencies in $(\pi\text{-}C_5H_5)Mo(CO)_2(\pi\text{-}C_3H_5)$ and similar species is due to the presence of *cis* and *trans* isomers based on a piano stool arrangement of the allyl ligand and the two carbonyl groups about the $(\pi\text{-}C_5H_5)Mo$ moiety. We present evidence which shows that for $(\pi\text{-}C_5H_5)Mo(CO)_2(\pi\text{-}C_3H_5)$ a more reasonable interpretation is one involving a configurational equilibrium between species which in a formal sense could be regarded as conformers. We reject the presence of *cis* and *trans* isomers for the following reasons: (i) It seems unreasonable from steric considerations to have the π-C_3H_5 group occupying the *trans* positions, but even more unlikely for the case of the C_7H_7 group in $(\pi\text{-}C_5H_5)Mo(CO)_2(\pi\text{-}C_7H_7)$, which also shows four infrared-active carbonyl stretching modes. (ii) From numerous studies of the vibrational spectra of metal carbonyls, it is known that the interaction constants k_c and k_t between pairs of *cis* and *trans* CO groups obey the approximate relationship $k_t \approx 2k_c$.[7] This leads to a marked difference between the separation of the symmetric and antisymmetric stretching modes in the *cis* and *trans* isomers, contrary to that observed in this case. (iii) The variable-temperature nmr spectra of Figure 1 show quite clearly that at low temperature (*ca.* -10 to $-50°$) the interconversion is slow enough to distinguish two distinct π-allyl groups and that these become averaged to a spectrum typical of a π-allyl (*i.e.*, AA′BB′X) at $+130°$.

The temperature dependence was essentially[8] the same in $CDCl_3$ and C_6H_6 throughout the range from $+10$ to $+40°$. However, spectra could not be obtained over the entire range in chlorinated solvents because of rapid decomposition at temperatures greater than *ca.* $+50°$. It is clear that the averaging process at $+130°$

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[1] F. A. Cotton, J. W. Faller, and A. Musco, *Inorg. Chem.*, **6**, 179 (1967).

[2] K. Vrieze, C. MacLean, P. Cossee, and C. W. Hilbers, *Rec. Trav. Chim.*, **85**, 1077 (1966).

[3] (a) J. K. Becconsall, B. E. Job, and S. O'Brien, *J. Chem. Soc., Sect. A*, 423 (1967); (b) the broadening and partial collapse of the nmr spectra of $Pd(\pi\text{-}C_3H_5)_2$ in the incompletely averaged range (*ca.* $+30$–$70°$) was suggested to be due to the onset of the internal rotation mechanism. Since the limiting spectrum was not observed, no valid conclusions can be drawn but there is a remarkable similarity between this behavior and that for $(\pi\text{-}C_5H_5)Mo(CO)_2(\pi\text{-}C_3H_5)$.

[4] G. Wilke, B. Bogdanovic, P. Hardt, P. Heimbach, W. Keim, M. Kroner, W. Oberkirch, K. Tanaka, and D. Walter, *Angew. Chem. Intern. Ed. Engl.*, **5**, 151 (1966).

[5] *Cf.* the discussions of the article by G. Wilke, *et al.*, in "Proceedings of the 9th Robert A. Welch Conference on Chemical Research, Nov 15–17, 1965," especially those by F. A. Cotton, p 184.

[6] R. B. King, *Inorg. Chem.*, **5**, 2242 (1966).

[7] F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).

[8] Solvent shifts for the various environments were observed in these spectra.