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Tetrahedral and Pseudo-tetrahedral Complexes of Cobalt(II) with Trimethylamine N-Oxide

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The solution behavior of the complexes $Co(TMNO)_4X_2$ and $Co(TMNO)_2X_2$ (where TMNO = trimethylamine N-oxide and $X^- = Cl^-, Br^-, I^-$, and SCN^-) have been examined in acetonitrile and methylene chloride. The stability of the tetrahedral species $Co(TMNO)_4^{2+}$ is demonstrated in these solvents and in the presence of excess TMNO by nmr and electronic absorption spectroscopy. The extent of displacement of X by TMNO is seen to vary with a change in X and a change of solvent in qualitative accord with predictions of the coordination model. The nmr isotropic shifts of the $Co(TMNO)_2X_2$ complexes are reported. The observed trend correlates with that predicted by a previously reported molecular orbital model. In spite of the bulky nature of TMNO, the trend is not in the direction predicted by a model based on steric effects. The absorption spectra of these complexes are seen to obey the "average environment" rule in spite of the detection of lower symmetry components of the transitions at low temperature. The calculated spin-orbit coupling parameter, λ', is not well behaved.

Introduction

In a previous article from this laboratory, we reported the contact shifts for the complexes CoL_2X_2 (L = pyridine and X = chloride, bromide, and iodide).[2] These shifts were interpreted in terms of a molecular orbital model, which essentially states that as the covalency (or amount of charge transfer) in the metal–X bond increases, the formal positive charge on the metal decreases, and hence covalency in the metal–L bond decreases. This interpretation has subsequently been challenged,[3] with the observed trends being attributed to a steric effect. In a rebuttal[4] several flaws in the steric agreement are noted and a complex was prepared in which there is a steric effect. We have been able to show that large steric effects caused a contact shift change in a direction *opposite* to that predicted[3] by the "steric model." Although there are several complexes in which the observed contact shifts are not in the direction predicted by our model, the complexes contain ligands L and X which are quite dissimilar (*i.e.*, their *Dq* values and π-bonding properties are very different). It is possible that pseudo-contact and/or large π-bonding effects are complicating the interpretation of the shifts in these complexes. The mo model is not claimed to be the only factor needed to predict the shift, and in some complexes the trend in the shifts may be dominated by other effects. Consequently, it was of interest to examine more complexes of the general formula CoL_2X_2, in order to test the limitations and predictive power of the molecular orbital model.[2] The TMNO (TMNO = trimethylamine N-oxide) complexes are particularly interesting because of the large *Dq* of TMNO and the bulky nature of this ligand.

In this article we report a complete study of a series of compounds of the general formula $Co(TMNO)_2X_2$ (X = halide, thiocyanate). The electronic spectra of the complexes are examined in detail to establish the nature of the species in solution. In addition to gaining further support for our molecular orbital model, the collected data provided checks on the "average environment rule" for pseudo-tetrahedral cobalt(II) systems.[5] Since it has been shown that the ligand field strength for TMNO is greater than those of the halogens,[6-8] such compounds offer a good check on the widespread applicability of the principle of average environments and on our molecular orbital model.

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[1] Abstracted in part from the Ph.D. thesis of D. W. Herlocker, University of Illinois, 1966; NSF Co-op Fellow, 1964–1966.

[2] B. B. Wayland and R. S. Drago, *J. Am. Chem. Soc.*, **88**, 4597 (1966).

[3] G. N. LaMar, *Inorg. Chem.*, **6**, 1939 (1967).

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[5] F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 4690 (1961).

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[7] After our initial report concerning the spectrochemical parameters of TMNO, it was found that the intensities but not the positions of the electronic transitions in $Co(TMNO)_4^{2+}$ varied with concentration of the complex and with the addition of excess TMNO in nitromethane. Thus the parameters were recalculated in acetonitrile solutions. The values obtained ($Dq = 476 \pm 5$ cm^{-1}, $B' = 771 \pm 12$ cm^{-1}, and $\beta = 0.79 \pm 0.02$) are within the error limits of those reported earlier.[6]

[8] D. W. Herlocker, to be submitted for publication.

We are also interested in the mechanisms of and exchange parameters for the exchange reactions of coordinated and bulk ligands in the CoL_2X_2 series of complexes. Previous articles have investigated the exchange reactions of α-picoline[9] and hexamethylphosphoramide (HMPA, $O{=}P[N(CH_3)_2]_3$)[10] in chloroform as a solvent. For these exchange studies to be valid, the CoL_2X_2 species must be stable in the presence of excess ligand. We have examined the behavior of $[Co(TMNO)_2X_2]$ species under these conditions.

Experimental Section

Materials.—Trimethylamine N-oxide dihydrate ($TMNO \cdot 2H_2O$) was obtained commercially from Eastman Organics and was used for synthetic purposes with no prior purification. The anhydrous material (TMNO) was obtained by subliming the dihydrate twice at reduced pressure at about 100°. The product was then stored in a dry-atmosphere box, in which all manipulations with the anhydrous material were performed. Hydrated cobalt(II) bromide was obtained from Alfa Inorganics and anhydrous cobalt(II) thiocyanate from City Chemical Co. The preparation of anhydrous cobalt(II) iodide has previously been described.[11] Eastman Spectrograde acetonitrile and Fisher reagent dichloromethane were stored over Linde 4-A Molecular Sieves for several days prior to use. Eastman practical grade triethyl phosphate was distilled under reduced pressure from barium oxide and stored in a desiccator over Linde 4-A Molecular Sieves when not in use. Glass wool was added to the flask to reduce bumping during the distillation. All other materials were of reagent grade and were used without further purification.

Preparation of Complexes. Tetrakis(trimethylamine N-oxide)-cobalt(II) perchlorate was prepared as previously described.[6]

Dihalobis(trimethylamine N-oxide)cobalt(II).—Anhydrous cobalt(II) halide was suspended in 35 ml of ethanol, and to this solution a stoichiometric amount of $TMNO \cdot 2H_2O$ dissolved in ethanol was added. The purple solution was stirred for 1 hr, with addition of several hundred milliliters of ether resulting in the formation of purple powders (the iodide has a bluish tinge). After a stirring period of 15 min, the compounds were filtered in a dry-atmosphere box, washed with ether, and dried under vacuum. The chloride complex is the only one which is appreciably hygroscopic. *Anal.* Calcd for $C_6H_{18}CoN_2O_2Cl_2$: C, 25.71; H, 6.42; N, 10.00. Found: C, 25.22; H, 6.37; N, 9.47. Calcd for $C_6H_{18}CoN_2O_2Br_2$: C, 19.52; H, 4.88; N, 7.59. Found: C, 19.45; H, 5.07; N, 7.13. Calcd for $C_6H_{18}CoN_2O_2I_2$: C, 15.55; H, 3.89; N, 6.05. Found: C, 15.61; H, 4.01; N, 5.42.

Bis(thiocyanato)bis(trimethylamine N-oxide)cobalt(II).—Anhydrous cobalt(II) thiocyanate (2 g) was dissolved in 40 ml of hot ethanol and filtered warm into a solution of $TMNO \cdot 2H_2O$ (2.5 g) in 25 ml of hot ethanol. A purple solution and purple precipitate were obtained. Stirring continued for 0.5 hr as the solution cooled, at which time ether was added to complete the precipitation. The compound was filtered, washed with ether, and dried under vacuum overnight. It is not hygroscopic. *Anal.* Calcd for $C_8H_{18}CoN_4O_2S_2$: C, 29.54; H, 5.54; N, 17.23. Found: C, 29.84; H, 5.83; N, 17.07.

The preparations of the $Co(HMPA)_2X_2$,[12] $Co(C_5H_5N)_2X_2$,[13] and $Co[(C_6H_5)_3P]_2X_2$ (X = halide,[14] thiocyanate[15]) complexes have previously been described.

Physical Measurements.—The results from conductance, spectral, magnetic, and nuclear magnetic resonance studies are listed in Table I–VI and in Figure 1. Electronic spectra were obtained on a Cary 14 spectrophotometer. For the electronic spectra of solutions containing an excess of the ligand, the reference solutions contained an equivalent amount of dissolved ligand. Solid-state electronic spectra of mulls were also obtained on the Cary 14.[16] The solid-state magnetic moments were obtained as previously reported.[6]

TABLE I

CONDUCTANCE DATA FOR $Co(TMNO)_2X_2$ COMPLEXES AND $[Co(TMNO)_4](ClO_4)_2$ IN ACETONITRILE

X^-	Concn, *M*	Concn of added ligand, *M*	Λ_M, ohm^{-1}	Temp, °C	Type of conductor
Cl^-	8.67×10^{-3}	. . .	13	27.2	Non
Cl^-	2.20×10^{-3}	0.0779	167	28.0	1:1
Br^-	3.26×10^{-3}	. . .	21	31.6	Non
Br^-	2.14×10^{-3}	0.0300	264	28.2	2:1
I^-	4.38×10^{-3}	. . .	58	27.6	"Non"
I^-	3.45×10^{-3}	0.2201	254	27.8	2:1
SCN^-	3.02×10^{-3}	. . .	22	24.8	Non
SCN^-	2.26×10^{-3}	0.0804	270	26.4	2:1
$[Co(TMNO)_4]$-$(ClO_4)_2$	1.61×10^{-3}	. . .	336	26.2	2:1
$Co(HMPA)_2Cl_2$	5.02×10^{-3}	. . .	13	27.2	Non
$[(C_2H_5)_4N]$-(ClO_4)	7.10×10^{-3}	. . .	156	26.0	1:1
$Co(HMPA)_4$-$(ClO_4)_2$	5.40×10^{-3}	. . .	261	27.5	2:1

The solution magnetic moments were obtained using a variation of a method proposed by Evans.[17] Into a standard nmr tube (5-mm o.d., 4-mm i.d.) was passed an inner tube (3-mm o.d., 2-mm i.d.), sealed on the bottom such that a thick piece of glass resulted. The outer tube had an opening constricted such that the inner one *just* passed through. The combination of the glass on the bottom and the constriction caused the inner tube to rise reasonably concentrically within the outer tube. The inner tube, which was about 4 mm longer than the outer tube, was held in place by a plastic nmr cap and rubber jackets such that both tubes were sealed from one another and the atmosphere. Assemblies are now available commercially from Wilmad Glass Co., Buena, N. J.

The sample solution (0.03–0.05 *M*) containing TMS was placed in the outer tube, while a solution of TMS in the solvent was placed in the inner tube. While no change in the results was noted if the order was reversed, it was easier to determine the position of the "paramagnetic" TMS peak with the sample in the outer tube, since in this case more of the solution was in the magnetic field.

The samples are spun in an A-60 spectrometer at the normal rate for 5 min until the tubes have attained temperature equilibrium with the magnet. The frequency difference between the TMS peaks (40–50 cps) is then measured accurately on the 50-cps scale. While the frequency difference of the TMS peaks is independent of the spinning rate, we have found that extraneous spinning side bands, which sometimes interfere with the reading, can be removed from the area by an increase in the spinning rate. Diamagnetic corrections[18] were then applied to the magnetic susceptibilities obtained for the TMNO complexes.

Room-temperature (32 ± 2°) nuclear magnetic resonance spectra of the $Co(TMNO)_2X_2$ complexes were obtained on a Varian DP-60 recording spectrometer using tetramethylsilane as an internal standard. The spectra obtained were calibrated with a side-band oscillator. Spectra for the $Co(TMNO)_4{}^{2+}$ complex

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[10] S. S. Zumdahl and R. S. Drago, submitted for publication.

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TABLE II

SPECTRAL DATA FOR $Co(TMNO)_2X_2$ COMPLEXES AND $[Co(TMNO)_4](ClO_4)_2$

X^-	Solvent	$\lambda\ (\epsilon)$[a]			
Cl^-	Mull	430 sh[c]	530	598, 620[b]	695
		1265			
	CH_2Cl_2	576 (222)	610 (350)	640 (315)	664 (340)
		1315 (67.3)	1425 (68.0)	1600 (61.0)	
	CH_3CN	580 sh (227)	610 (330)	635 (310)	665 (318)
		1335 (64.9)	1435 (68.3)	1595 (58.9)	
Br^-	Mull	431 sh	520	557 sh	598
		625 sh	715	1260	
	CH_2Cl_2[d]	590 sh	625	652	674
	CH_3CN	590 sh	625 (355)	651 (315)	680 (300)
		1335 (70)	1475 (71)		
I^-	Mull	442 sh	520	585 sh	627
		651 sh	750	1340	
	CH_2Cl_2[d]	600	646	670	705
	CH_3CN	592 (280)	644 (410)	. . .[e]	720 (245)
		1340 (83)	1475 (76)		
	$CH_3CN + I^-$[f]	596 (287)	643 (389)	680 (322)	712 (296)
		1350–1500 (85)[g]			
SCN^-	Mull	495	586	657	1235
		1385			
	CH_2Cl_2	555 sh	587 (520)	625 (585)	
	CH_3CN	555 sh	587 (530)[b]	598 (530)[b]	622 (560)
		1225 (160)			
$[Co(TMNO)_4]$-$(ClO_4)_2$	Mull		566	1075	1400
	CH_3CN	535 sh	567 (289)	1100 (77)	1405 (55)

[a] Wavelength in mμ; ε in M^{-1} cm². [b] Poorly resolved doublet. [c] sh = shoulder. [d] Saturated solution. [e] This transition was not observed. [f] The iodide ion is added as $[(n\text{-}C_4H_9)_4N]I$ (0.0114 M complex and 0.0239 M iodide). [g] The absorption is very broad.

TABLE III

SPECTRAL DATA FOR $Co(TMNO)_2X_2$ COMPLEXES AND $[Co(TMNO)_4](ClO_4)_2$

X^-	Solvent	C, M	$\lambda\ (\epsilon)$			
Cl^-	0.8549 M TMNO in CH_2Cl_2	0.0093	560 sh[a]	593 (300)	614 (290)	
Cl^-	0.3896 M TMNO in CH_3CN	0.0110	550 sh	590 (275)	630 sh	1190 (68.5)
			1400 (61.4)			
Br^-	0.1500 M TMNO in CH_3CN	0.0107	535 sh	568 (292)	1100 (73.9)	1400 (55.3)
I^-	0.1171 M TMNO in CH_3CN	0.0047	535 sh	569 (294)	1100 (76.2)	1400 (55.5)
SCN^-	0.4022 M TMNO in CH_3CN	0.0113	535 sh	570 (288)	1100 (75.3)	1400 (55.6)
$[Co(TMNO)_4](ClO_4)_2$	TMNO[b] in CH_3CN	. . .[b]	535 sh	567 (296)	1095 (77)	1400 (53)

[a] sh = shoulder. [b] A variety of concentrations of complex and added ligand were studied.

TABLE IV

AVERAGE ENVIRONMENT CALCULATIONS FOR $Co(HMPA)_2X_2$ AND $Co(TMNO)_2X_2$ COMPLEXES (cm^{-1})

Complex	Dq(calcd)	B′(calcd)	Dq(obsd)	B′(obsd)
$Co(TMNO)_2Cl_2$	394	746	393	748
$Co(TMNO)_2Br_2$	384	735	391	719
$Co(TMNO)_2(NCS)_2$	466	711	462	734
$Co(HMPA)_2Cl_2$	328	764	325	777
$Co(HMPA)_2Br_2$	318	753	317	761
$Co(HMPA)_2I_2$	310	725	316	739
$Co(HMPA)_2(NCS)_2$	400	748	395	757
$[Co(TMNO)_4]^{2+}$			476	771[a]
$[Co(HMPA)_4]^{2+}$			344	807[b]
$[CoCl_4]^{2-}$			311	720[c]
$[CoBr_4]^{2-}$			292	699[c]
$[CoI_4]^{2-}$			276	642[c]
$[Co(NCS)_4]^{2-}$			455	691[c]

[a] This work. [b] Data from ref 6. [c] Data from ref 5. This is the average value of results in $CHCl_3$, CH_2Cl_2, and CH_3NO_2 solutions.

TABLE V

SHIFTS FOR SOME TRIMETHYLAMINE N-OXIDE COMPLEXES OF COBALT(II)

Species	Obsd shift,[a] Hz	Species	Obsd shift,[a] Hz
$Co(TMNO)_2Cl_2$	−462 ± 10	$Co(TMNO)_2(NCS)_2$	−570 ± 10
$Co(TMNO)_2Br_2$	−515 ± 10	$[Co(TMNO)_4]^{2+}$	−615 ± 10

[a] Observed shift = $\delta_{\text{complex}} - \delta_{\text{ligand}}$.

and TMNO in acetonitrile were obtained on the Varian A-60 spectrometer.

Results

Conductance values for $[Co(TMNO)_4](ClO_4)_2$ and the $[Co(TMNO)_2X_2]$ complexes are presented in Table I. Spectral results in acetonitrile and dichloromethane are recorded in Tables II (no added TMNO) and III (added TMNO). Average environment calculations for some CoL_2X_2 complexes are reported in

Table VI

Magnetic Data

Compound	$10^6\chi_{\text{measd}}$, cgsu	$10^6\chi_M^{\text{cor}}$, cgsu	Temp, °K	μ_{eff},[d] BM
$Co(TMNO)_2Cl_2$	32.5933	9249	299	4.71 ± 0.06
$Co(TMNO)_2Br_2$[c]	25.0699	8870	299.5	4.77 ± 0.06[c]
$Co(TMNO)_2I_2$	21.0411	9927	299	4.88 ± 0.06
$Co(TMNO)_2(NCS)_2$	25.6723	8473	299	4.54 ± 0.06
$Co(TMNO)_2(NCS)_2$	23.74	7844	307	4.40 ± 0.06[a]
$[Co(TMNO)_4](ClO_4)_2$	15.2863	8748	292	4.54 ± 0.06
$Co(HMPA)_2Br_2$	16.02	9584	305.5	4.87 ± 0.06[b]

[a] Data obtained from acetonitrile solutions. [b] Data obtained from dichloromethane solution. [c] A value of 4.7 was obtained from measurements in CH_3CN. [d] Unless indicated data were obtained on the solid.

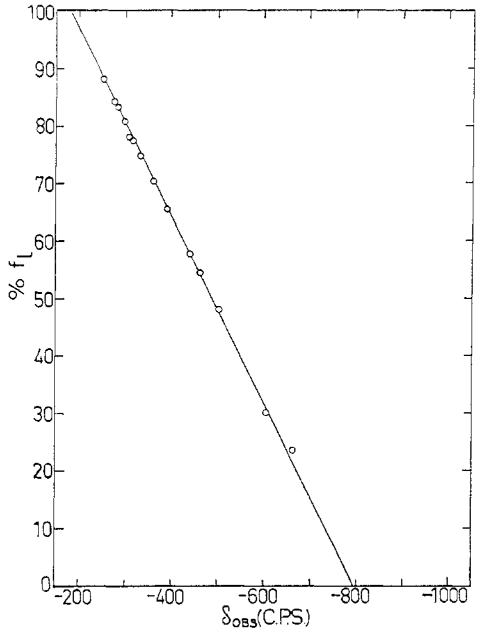

Figure 1.—Observed nuclear magnetic resonance frequencies of the proton in $Co(TMNO)_4^{2+}$ as a function of the mole percentage of "free" TMNO protons in the system.

Table IV. Nmr shifts and magnetic susceptibilities for the complexes are presented in Tables V and VI, respectively.

The determination of χ_M' for the complexes in solution is obtained from

$$\chi_M' = \frac{3\Delta\nu(\text{mol wt})}{2\pi\nu C} + \chi_D \qquad (1)$$

where $\Delta\nu$ is the difference in resonance frequency of the TMS peaks ("diamagnetic" and "paramagnetic") in Hz, ν is the frequency of the probe (60×10^6 Hz), C is the concentration of the complex in g/ml of solution, and the other terms have their usual significance. We have not found it necessary to utilize the correction terms mentioned by Evans.[17]

The $Co(TMNO)_4^{2+}$ shift was determined from the intercepts of a plot of average chemical shift *vs.* mole fraction of free ligand for mixtures of the complex and excess TMNO (Figure 1). The value of δ_e obtained from the graph agrees within experimental error with that obtained from the spectrum of TMNO in acetonitrile. The linearity of this plot over the range of 20–90% free ligand is an excellent indication of the presence of only one complex, the tetrahedral $Co(TMNO)_4^{2+}$ one, in this system.[19] This result is in agreement with spectral data, which indicate no change in species present upon the addition of excess base (Tables II and III).

The shifts for the pseudo-tetrahedral complexes could not be obtained by this procedure because they reacted with excess TMNO, forming other complexes (see Tables I–III). Since the resonances are very broad (the half-widths at half-heights of the resonances are at least 200 Hz) and since the solubilities of the complexes in acetonitrile are low, data for these complexes were obtained with a DP-60 spectrometer, using saturated solutions of the complexes. The concentration of saturated solution of $Co(TMNO)_2I_2$ in acetonitrile (with approximately a 2:1 excess of added iodide ion to prevent dissociation) was too dilute to give an observable signal.

The error limits assigned to the shifts for the pseudo-tetrahedral species arise because of the difficulty in locating the centers of the broad proton resonance absorptions. Because of this problem, the resonances were observed at least four times with an average then being taken of those values. A dilution of the most soluble complex, $Co(TMNO)_2Cl_2$, to half its original concentration resulted in no change within experimental error in the shift. Spectra could not be obtained for more dilute solutions of the less soluble bromide and thiocyanate complexes.

Discussion

Solution Behavior of Complexes.—The conductance and spectral data for $[Co(TMNO)_4]X_2$ (Tables I–III) indicate that these complexes are 2:1 electrolytes in acetonitrile, with the ligand field around the cobalt(II) ion being tetrahedral in nature. The equivalence of the electronic spectra in the absence and presence of added TMNO indicates that neither a tetrahedral ⇄ octahedral equilibrium nor acetonitrile solvation is occurring. These ideas are in agreement with the nmr data graphed in Figure 1, in which only one species plus excess ligand appears to be present over a wide range of complex and added ligand concentrations.

The multistructured absorptions in the visible and near-infrared regions of the electronic spectrum (Table II) and the magnitudes of the extinction coefficients for the bis complexes are indicative of pseudo-tetrahedral cobalt(II).[5] The low conductance values for the complexes in acetonitrile, the general similarities of the solution electronic spectra in dichloromethane and acetonitrile, and the relative invariance of the extinction coefficients over a fairly wide concentration range (when applicable) indicate that only very small changes occur in the ligand fields about the cobalt(II) ion under these conditions, and consequently no extensive ligand displacement by acetonitrile is noted.

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(19) This plot was obtained by using a number of different complexes containing the $Co(TMNO)_4^{2+}$ cation with various anions in acetonitrile and dichloromethane (where possible) solutions. The linearity of the plot precludes any solvent or anion reactions with the cation. The various $Co(TMNO)_4^{2+}$ complexes will be discussed further in ref 8.

As noted from both conductance and spectral data (Tables I and II), some dissociation does occur in the iodide complex in acetonitrile. Addition of excess iodide ions (at an iodide to complex ratio of about 2:1) produces an electronic spectrum which is quite similar to that of the complex dissolved in dichloromethane (Table II), supporting the idea that the acetonitrile is simply displacing some iodide ions from the coordination sphere of the complex.

Previous studies on CoL_2X_2 species (L = HMPA,[20] pyridine,[21] quinoline and isoquinoline,[22] and 2- and 4-methylpyridine[21,23] in the presence of added base have shown that a variety of products of general formula $[CoL_4X_2]$, $[CoL_3X]X$, and $[CoL_4]X_2$ can be formed. It has also been shown, however, that some of the above species undergo no displacement reaction with added base, thus being amenable to nmr exchange rate studies. Since TMNO has such a high *Dq* toward tetrahedral cobalt(II), and since it is a rather bulky ligand, it would have been of interest to evaluate the kinetic parameters for the ligand displacement reaction in a poorly coordinating solvent. In this connection the solution behavior of the $[Co(TMNO)_2X_2]$ complexes in the presence of excess TMNO was investigated.

Addition of large amounts of excess TMNO increases the conductance values of the complexes to those of 1:1 (chloride) and 2:1 (bromide, iodide, and thiocyanate) electrolytes (Table I). The electronic spectral data for the bromide, iodide, and thiocyanate complexes are identical with those for a known $[Co(TMNO)_4]^{2+}$ complex (Table II). The nmr shift of the protons of the thiocyanate complex (with added TMNO in acetonitrile) falls on the linear mole fraction plot for the $[Co(TMNO)_4]^{2+}$ species (Figure 1). Thus for these three complexes, the following reaction of the complexes with excess TMNO in acetonitrile solutions is proposed

$$Co(TMNO)_2X_2 + 2TMNO \xrightarrow{CH_3CN} Co(TMNO)_4^{2+} + 2X^- \quad (2)$$

($X^- = Br^-, I^-, NCS^-$).

The conductance and spectral changes for solutions of $Co(TMNO)_2Cl_2$ with added TMNO in acetonitrile indicate the reaction

$$Co(TMNO)_2Cl_2 + TMNO \xrightarrow{CH_3CN} Co(TMNO)_3Cl^+ + Cl^- \quad (3)$$

Changes (different from those noted in acetonitrile solutions) are also observed in the electronic spectrum of dichloromethane solutions of the chloride complex in the presence of added TMNO. Since the center of gravity of the visible band in dichloromethane is at a lower energy than that in acetonitrile, a weaker average ligand field is present around the cobalt(II) ion in the former solution, indicating less ligand displacement in the dichloromethane solution. Clearly, then, the $Co(TMNO)_2X_2$ complexes do not lend themselves to the study of ligand-exchange reactions by nmr line-broadening techniques.

The above results are qualitatively consistent with the coordination model[24] description of nonaqueous solvent behavior. This model predicts that the iodide ion, which is more weakly bound than the chloride ion, is more susceptible to displacement by another donor (in this case TMNO). It also emphasizes the importance of solvating properties of the solvent as an aid in determining the amount of anion displacement. In the above studies more extensive displacement of the chloride ion from $Co(TMNO)_2Cl_2$ by TMNO was observed in the more polar, better solvating acetonitrile than in the less polar, more poorly solvating dichloromethane.

Nmr Isotropic Shifts.—Trimethylamine N-oxide is an interesting ligand for contact shift studies, in that there are no π bonds in the molecule. Consequently, any spin delocalization which may occur onto the ligand will involve only σ ligand orbitals. The observed downfield shifts for the protons (Table V) in both the C_{2v} complexes CoL_2X_2 and the T_d complex $Co(TMNO)_4^{2+}$ are consistent with a σ-delocalization mechanism. The large magnitudes of the shifts noted for the methyl protons in $Co(TMNO)_4^{2+}$, which are far removed from the donor atom, are also consistent with considerable mixing of the metal and ligand orbitals.

Although the differences in the shifts for the chloride and bromide complexes are not very large, they are in a direction consistent with the mo model previously proposed.[2] In the $Co(TMNO)_2(NCS)_2$ and $Co(HMPA)_2(NCS)_2$ complexes,[2] the shifts are larger than those in the analogous halide complexes. This is in the opposite direction of that predicted by the steric model.[3] This increase can be rationalized by proposing that metal–anion back-bonding increases the formal positive charge on the metal, thus increasing the covalency in the metal–ligand bond. Because of the possible contributions to the observed isotropic shifts from pseudo-contact shifts, however, it is probably not prudent at this time to do much more than to observe the qualitative consistency of these results with the molecular orbital model[2] and with the observed shifts in the analogous pyridine complexes.

Average Environment Calculations.—The spectral data collected for the CoL_2X_2 (L = TMNO, HMPA) complexes provide an interesting test of the average environment rule,[5] because the *Dq* of TMNO is much larger than those of the halide ions while that of HMPA is similar to that of the halogens.[12] Any splittings in the spectral bands from a C_{2v} component arising from a large difference in *Dq*'s of the coordinated ligands would thus be more noticeable in the TMNO complexes. The results of these average-field calculations are presented in Table IV, using solution values in all instances. In view of the complexity of this problem, surprisingly good agreement between the calculated and observed

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values of Dq and B' is observed. These results, in addition to those reported by Cotton, *et al.*,[5] and by Madan, *et al.*,[25,26] for sulfur donors, illustrate that this concept is valid for a large number of pseudo-tetrahedral cobalt(II) complexes.[27-29] This agreement is indeed surprising because low-temperature mull spectra exhibit splitting of the near-infrared band greater than can be expected from spin–orbit coupling suggesting a low-symmetry component. The high-energy band has at least six components.

Solid-State Behavior of the Complexes.—While the solid-state and solution electronic spectral data for $Co(TMNO)_4^{2+}$ are essentially identical, there are differences in the same sets of data for the $Co(TMNO)_2X_2$ complexes (Table II). While the moments are in the range expected for tetrahedral cobalt(II) (Table VI), with the exception of the thiocyonate complex, values calculated for λ' (after correcting for TIP[5]) are higher than those normally calculated for tetrahedral cobalt(II) complexes,[5] being even higher than the gas-phase value. This indicates inappropriate use of the model for T_d complexes on these lower symmetry complexes and renders the interpretations of λ' values for other than T_d complexes questionable. Even then, accurate magnetic moments are needed. The λ' value for the $Co(TMNO)_4^{2+}$ species (-158 cm^{-1}) is in the normal range[5] of 130–170 cm^{-1} usually encountered.

In other pseudo-tetrahedral cobalt(II) complexes of the type CoL_2X_2 (L = pyridine, HMPA, triphenylphosphine) it was found that the positions of maximum absorbance did not change upon change of state. The spectral data are not indicative of halide bridging, as is the case with $Co(py)_2Cl_2$ (py = pyridine),[13] but evidently lattice effects are causing changes in the ligand fields around the cobalt(II) ion.

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Gas-Phase Enthalpies of Adduct Formation: Dimethylamine–Chloroform and Ethyl Acetate–Boron Trifluoride

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The gas-phase thermodynamic data for formation of the adduct of ethyl acetate with boron trifluoride and for the hydrogen-bonding interaction of chloroform with dimethylamine are reported. For the chloroform–dimethylamine adduct an enthalpy of dissociation, $\Delta H_D = 5.8 \pm 1.1$ kcal/mol, and an entropy of dissociation, $\Delta S_D = 22.5$ eu, were obtained. Values of $\Delta H_D = 12.8 \pm 0.7$ kcal/mol and $\Delta S_D = 37$ eu were obtained for the ethyl acetate–boron trifluoride adduct. Toward chloroform, dimethylamine is a stronger donor than triethylamine. Previously,[4] we have been able to assign two parameters to an acid, E_A and C_A, and two to a base, E_B and C_B, which when substituted into the following equation reproduce the enthalpy of adduct formation: $-\Delta H = E_AE_B + C_AC_B$. The systems reported here have been incorporated into this correlation and some interesting insight into the existence of steric effects in the donor–acceptor interactions is provided.

Introduction

In contrast to the many studies on donor–acceptor interactions in solution, relatively little work has been reported on such systems in the gas phase. Limitations on volatility of reactants and adducts, difficulties in purchasing or constructing the requisite high-vacuum equipment, and operational problems all mitigate against gas-phase measurements when other methods are available. Yet gas-phase thermodynamic data are singularly important, particularly for testing the common assumption that solvation effects can be neglected (here, specifically, for donor–acceptor interactions) if a nonpolar solvent is employed. These studies were initiated, in part, to provide a test for this assumption. At that time we knew of no studies providing reliable thermodynamic data for adduct formation both in the gas phase and in solution. Subsequent to the completion of this work, reports appeared[2,3] indicating that similar enthalpies are obtained in the gas phase and in carbon tetrachloride or hexane solution. This evidence supported the use of data obtained in these nonpolar solvents along with gas-phase data for correla-

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