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Complexes of Substituted Benzothiazoles. 3. Cobalt(II) Complexes of the 'tripod' Ligand Tris(2-benzothiazolylmethyl)amine

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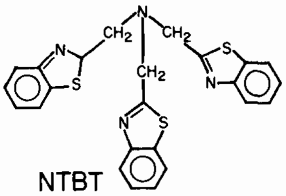
Tetradentate 'tripod' ligands are often capable of forcing transition metal ions to adopt a trigonal bipyramidal stereochemistry by virtue of their own geometrical constraints and the bulk of the pendant groups. The tetradentate 'tripod' ligand tris(2-benzothiazolylmethyl)amine (NTBT) has been found to form only two trigonal bipyramidal cations, $[Co(NTBT)X]^+$ (X = Cl, Br), present in the complexes $[Co(NTBT)X]BPh_4\cdot(CH_3CN)_2\cdot yH_2O$ (X = Cl, y = 0.5, X = Br, y = 0), $[Co(NTBT)X][CoX_3(CH_3CN)](CH_3CN)$ (X = Cl, Br) and $[Co(NTBT)Br]_2[CoBr_4]\cdot(MeNO_2)_2\cdot1.5EtOH$. Coordinated acetonitrile occurs in two of the mixed stereochemistry systems, but rather than occupying an axial site in the trigonal bipyramidal cation it appears to be coordinated at the tetrahedral centre. Pseudo-octahedral structures exist in the solid state in all the other systems investigated, i.e. $Co(NTBT)Cl_2\cdot2H_2O$, $Co(NTBT)Br_2\cdot(CH_3CN)_2$, $[Co(NTBT)(NCS)_2]$, $[Co(NTBT)(NO_3)]NO_3\cdot H_2O$, $[Co(NTBT)(H_2O)_2](ClO_4)_2$. The complex $Co(NTBT)Br_2\cdot(CH_3CN)_2$, which is octahedral in the solid state, dissociates in solution in nitromethane to form the cation $[Co(NTBT)Br]^+$. Structural assignments are supported by ligand field and infrared spectra and magnetism and conductance data.

Introduction

Recent studies have indicated the facility with which trisubstituted amines, in which the substituent groups comprise amines, benzimidazole and benzothiazole, can force certain first row transition metal ions to adopt five-coordinate trigonal bipyramidal stereochemistries [1–9]. The symmetrical 'tripod' nature of these ligands, in many cases, imparts three fold symmetry to the complex itself but octahedral derivatives are also obtained, in certain cases, *e.g.* with the 'tripod' ligands tris(2-benzimidazolylmethyl)amine (NTB) [7, 8] and tris(2-benzothiazolylmethyl)amine (NTBT) [9]. In particular this is so in the case of nickel complexes of NTB, all of which appear to be octahedral [7]. Factors which influence the formation of five- or six-coordinate derivatives include the steric bulk of the pendant groups and the electron configuration of the metal ion. Thermochemical studies on the formation of five-coordinate derivatives of the type [M(trenMe)Br]Br (M = Mn → Zn) have shown that enthalpy changes for these systems are much less than those involved in the formation of similar octahedral derivatives *e.g.* $[M(dien)_2]^{2+}$, $[M(en)_3]^{2+}$ [10]. As a consequence, unless the ligand can exert a strong stereochemical influence on the metal ion by virtue of its own geometry and the steric bulk of the pendant groups then the formation of six-coordinate derivatives is quite likely. In the case of nickel(II) derivatives the preference for six-coordinate species over five-coordinate systems is much more marked than is the case for cobalt(II) and copper(II) [10].



NTBT

Fig. 1. 'Tripod ligand'.

In the present study we have examined the coordinating ability of the 'tripod' ligand tris(2-benzothiazolylmethyl)amine (NTBT, Fig. 1) towards cobalt (II) salts. Surprisingly, many of the complexes have octahedral stereochemistries, while for the other species trigonal bipyramidal structures exist. The structural similarity between NTBT and its benzimidazole analogue NTB, which forms only trigonal bipyramidal cobalt complexes, might have suggested a preference for five-coordination with this system. No evidence exists for S coordination and the 'tripod' ligand is assumed to behave as an N_4 donor in all cases. A recent X-ray structure on the system $[Cu(NTBT)(NO_3)]NO_3\cdot0.5H_2O$ [9] reveals a somewhat distorted trigonal bipyramid in which NTBT behaves as an N_4 donor and the fifth coordination site is occupied by a monodentate nitrate group.

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Experimental

Syntheses

NTBT was synthesized according to the procedure of Thompson *et al.* [9]. Hydrated or anhydrous metal salts were employed.

[Co(NTBT)X]BPh$_4$·(CH$_3$CN)$_2$·yH$_2$O (X = Cl, y = 0.5; X = Br, y = 0) (I, II).

NTBT (1.0 g, 2.2 mmol) was dissolved in refluxing acetonitrile (130 cm^3). NaBPh$_4$ (1.5 g, 4.1 mmol) was dissolved in warm acetonitrile and filtered into the NTBT solution. $CoCl_2 \cdot 6H_2O$ (0.52 g, 2.2 mmol) was dissolved in acetonitrile (20 cm^3 + 3 cm^3 triethyl orthoformate, TEOF) and added to the ligand solution. The mixture was refluxed for 15 min and allowed to stand for 1 h. The white solid which formed (NaCl) was filtered off and the volume of the mother liquor reduced to the point of crystallization. On standing at room temperature purple crystals were obtained. The product was recrystallized from acetonitrile/TEOF and dried under vacuum at room temperature.

The bromo complex was prepared in a similar fashion. Attempts to produce analogous compounds with *e.g.* X = NCS, I, were unsuccessful.

Co(NTBT)Cl$_2$·2H$_2$O (III), Co(NTBT)Br$_2$·(CH$_3$CN)$_2$ (IV), [Co(NTBT)(NCS)$_2$] (V).

These products were obtained by mixing acetonitrile solutions of the metal salt and ligand in a 1:1 stoichiometry, as described above, and recrystallizing the products from acetonitrile/TEOF. The complexes were dried under vacuum at room temperature.

[Co(NTBT)X][CoX$_3$(CH$_3$CN)]·CH$_3$CN (X = Cl, Br) (VI, VII).

These compounds were obtained by reacting a sixfold excess of metal salt with NTBT in acetonitrile, as described previously. However the dark blue crystals obtained were not recrystallized but were simply washed with acetonitrile and dried briefly under vacuum at room temperature.

Attempts to produce analogous compounds with *e.g.* X = NCS, I, were not successful. Although a dark blue product was obtained from the reaction of cobalt thiocyanate and NTBT in acetonitrile, in some reactions, it was always contaminated with [Co(NTBT)(NCS)$_2$]. Spectral data suggest this blue compound to be analogous to the chloro and bromo complexes.

[Co(NTBT)Br]$_2$[CoBr$_4$]·(MeNO$_2$)$_2$·1.5EtOH (VIII).

$CoBr_2 \cdot 6H_2O$ (5.0 g, 15 mmol) was dissolved in ethanol (100 cm^3), TEOF (10 cm^3) added and the mixture refluxed for 20 min. NTBT (0.75 g, 1.6 mmol) was dissolved in warm dichloromethane (80 cm^3) and the solution added slowly to the hot solution of cobalt bromide. The mixture was refluxed with stirring for 10 min and allowed to cool. Purple crystals formed which were recrystallized from nitromethane/TEOF and dried under vacuum at room temperature.

An analogous pale purple-blue chloro complex was prepared, but was too insoluble to purify successfully by recrystallization. Microscopic examination revealed the presence of a light coloured impurity, which could not be removed from the crude product and since meaningful analytical data were not obtained for this system it will not be discussed in detail.

[Co(NTBT)(NO$_3$)]NO$_3$·H$_2$O (IX), [Co(NTBT)(H$_2$O)$_2$](ClO$_4$)$_2$ (X).

NTBT (0.75 g, 1.6 mmol) was dissolved in dichloromethane (50 cm^3) and added to a solution of $Co(NO_3)_2 \cdot 6H_2O$ (2.5 g, 8.6 mmol) in methanol (40 cm^3). The resulting purple coloured solution was heated on a steam bath until pink crystals formed. After standing at room temperature the product was filtered, washed with methanol/ether (50/50), recrystallized from acetonitrile/TEOF and dried under vacuum at room temperature.

The perchlorate complex was prepared in a similar fashion using an excess of $Co(ClO_4)_2 \cdot 6H_2O$.

Analytical data for the complexes are given in Table I.

Physical Measurements

Electronic spectra were recorded on a Cary 17 spectrometer and infrared spectra were obtained with a Perkin-Elmer model 283 spectrometer. Magnetic suceptibilities were obtained at room temperature by the Faraday method with a Cahn model #7600 Faraday Magnetic Susceptibility system, coupled to a Cahn gram electrobalance and conductance data were obtained with a General Radio Company bridge with impedance comparator and a constant temperature bath adjusted to 25 °C. Microanalyses were carried out by the Canadian Microanalytical Service, Vancouver, and metal analyses were determined by Atomic Absorption with a Varian Techtron AA-5, after digestion of the samples in concentrated HNO_3 or *aqua regia*.

Results and Discussion

Ligand Field Spectra

In the solid state the complexes [Co(NTBT)X]·BPh$_4$·(CH$_3$CN)$_2$·yH$_2$O (X = Cl, y = 0.5; X = Br, y = 0) (I, II) are characterized by four absorptions in the range 5000–20000 cm^{-1}, typical of trigonal bipyramidal cobalt(II) systems (Table II, Fig. 2). Bertini and co-workers [11] attempted to simulate

TABLE I. Analytical Data.

Compound		Colour	Found (%)				Calcd. (%)			
			C	H	N	M	C	H	N	M
I	$[Co(NTBT)Cl]BPh_4\cdot(CH_3CN)_2\cdot0.5H_2O$	Purple-blue	64.7	4.34	8.50	6.2	64.8	4.67	8.73	6.0
II	$[Co(NTBT)Br]BPh_4\cdot(CH_3CN)_2$	Purple-blue	62.7	4.37	8.40	5.6	62.5	4.41	8.42	5.8
III	$Co(NTBT)Cl_2\cdot2H_2O$	Purple	46.2	3.01	8.85	9.0	46.2	3.52	8.97	9.4
IV	$Co(NTBT)Br_2\cdot(CH_3CN)_2$	Purple	44.3	3.10	10.8	8.0	44.3	3.16	11.0	7.8
V	$[Co(NTBT)(NCS)_2]$	Purple-pink	49.1	2.75	13.0	8.9	49.3	2.84	13.2	9.3
VI	$[Co(NTBT)Cl][CoCl_3(CH_3CN)]\cdot CH_3CN$	Blue	41.7	2.88	10.5	14.6	42.0	3.00	10.5	14.8
VII	$[Co(NTBT)Br][CoBr_3(CH_3CN)]\cdot CH_3CN$	Blue	34.1	2.07	8.49	11.8	34.3	2.45	8.58	12.1
VIII	$[Co(NTBT)Br]_2[CoBr_4]\cdot(MeNO_2)_2\cdot1.5EtOH$	Purple	36.0	2.57	7.97	9.7	36.0	2.89	7.94	10.0
IX	$[Co(NTBT)(NO_3)]NO_3\cdot H_2O$	Pink	43.7	2.81	12.7	8.7	43.7	3.03	12.7	8.9
X	$[Co(NTBT)(H_2O)_2](ClO_4)_2$	Pink	38.1	2.41	7.48	8.0	38.3	2.93	7.44	7.8

TABLE II. Electronic Spectra (cm^{-1}).*

(*a*) $[Co(NTBT)X]^{n+}$

Compound		$^4E \leftarrow {}^4A_2$	$^4E \leftarrow {}^4A_2$	$^4A_2(P) \leftarrow {}^4A_2$	$^4E(P) \leftarrow {}^4A_2$
I	$[Co(NTBT)Cl]BPh_4\cdot(CH_3CN)_2\cdot0.5H_2O$	d 5600 e 5900 (51)	11400 11800 (39)	15300 15700 (212)	19400 19600 (221)
II	$[Co(NTBT)Br]BPh_4\cdot(CH_3CN)_2$	d 5500 e 5500 (47)	11300 11500 (32)	15400 15800 (222)	19100 19200 (196)
IV	$Co(NTBT)Br_2\cdot(CH_3CN)_2$	e 5700 (41)	11500 (31)	15700 (223)	19100 (183)
VI	$[Co(NTBT)Cl][CoCl_3(CH_3CN)]\cdot CH_3CN$	d 5700 e	11900 11750 (52)		19600 19500 (240)
VII	$[Co(NTBT)Br][CoBr_3(CH_3CN)]\cdot CH_3CN$	d 5700 e	12000 11600 (32)		19400, 18500 19200 (203)
VIII	$[Co(NTBT)Br]_2[CoBr_4]\cdot(MeNO_2)_2\cdot1.5EtOH$	d e	11200 11500 (68)		19200 19200 (417)

(*b*) $[Co(NTBT)X_2]^{n+}$

Compound		$^4T_{2g} \leftarrow {}^4T_{1g}$ (ν_1)	$^4A_2 \leftarrow {}^4T_{1g}$ (ν_2)	$^4T_{1g}(P) \leftarrow {}^4T_{1g}$ (ν_3)	Dq	B	β
III	$Co(NTBT)Cl_2\cdot2H_2O$	d 7600	[15200]	17700	859	747	0.77
IV	$Co(NTBT)Br_2\cdot(CH_3CN)_2$	d 8100		18500	917	764	0.79
V	$[Co(NTBT)(NCS)_2]$	d 8300, [9100]	[15600]	18200	973	705	0.73
IX	$[Co(NTBT)(NO_3)]NO_3\cdot H_2O$	d 8600 e 8200 (12), 10700(10)	[15600] [15800] (25)	20000 [18800] (77), 20600(99)	969	843	0.87
X	$[Co(NTBT)(H_2O)_2](ClO_4)_2$	d 8300, [8800] e 7100 (12), 9500 (15)		20000, [21000] 18400 (118), 20000 (134), 21800 (124)	968	880	0.91

(*c*) $[CoX_4]^{2-}$

Compound		$^4T_1 \leftarrow {}^4A_2$ (ν_2)	$^4T_1(P) \leftarrow {}^4A_2(\nu_3)$
VI	$[Co(NTBT)Cl][CoCl_3(CH_3CN)]\cdot CH_3CN$	d [6500], 6700, [7400] e [6700] (88), 7500 (72)	15300, 16900 15500 (624), 16900 (460)
VII	$[Co(NTBT)Br][CoBr_3(CH_3CN)]\cdot CH_3CN$	d 5700, [6500] e [6500] (99), 6800 (85)	14300, 15600, 16100 14400 (640), 14900 (615), 15400 (605), 16100 (590)
VIII	$[Co(NTBT)Br]_2[CoBr_4]\cdot(MeNO_2)_2\cdot1.5EtOH$	d 5200, 5500 e 6300 (145)	13700, 14200, 14900, 15500 14400 (785), 15400 (887), 16100 (863)

*Labels mean the following: d, mull transmittance spectrum (room temperature); e, solution in nitromethane; [ ] shoulder, ( ) molar extinction coefficient. The $^4E \leftarrow {}^4A_2$ and $^4A_2(P) \leftarrow {}^4A_2$ transitions for the complexes $[Co(NTBT)X][CoX_3(CH_3CN)]\cdot CH_3CN$ (X = Cl, Br) appear to be buried for the most part under the ν_2 and ν_3 absorptions, respectively, associated with $[CoX_3(CH_3CN)]^-$

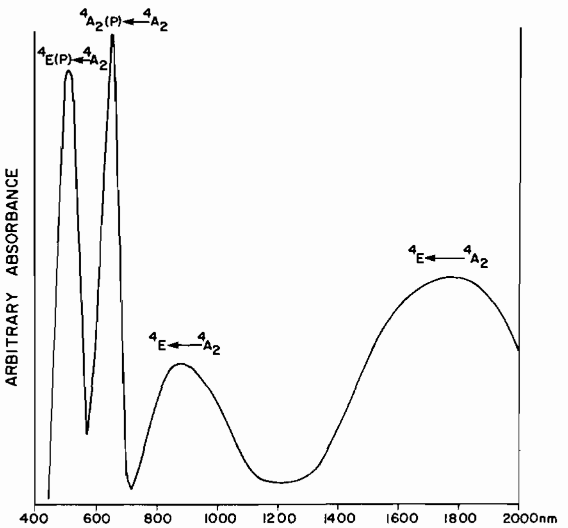

Fig. 2. Mull transmittance spectrum of [Co(NTBT)Cl] $BPh_4 \cdot (CH_3CN)_2 \cdot 0.5H_2O$.

the observed spectra of some pseudo-trigonal bipyramidal cobalt(II) complexes using both the crystal field and angular overlap approach. In the case of the complex [Co(trenMe)Br]Br (trenMe = tris(2-dimethylaminoethyl)amine), which has a tetrahedrally distorted trigonal bipyramidal structure [3] with an N_{ax}–Co–N_{eq} angle (α) of 81.1°, a good agreement was obtained between observed and calculated transition energies using a C_{3v} symmetry field. Four bands were observed in the diffuse reflectance spectrum of [Co(trenMe)Br]Br at 5700, 12300, 16100 and 19500 cm^{-1}, assigned to the transitions ${}^4E \leftarrow {}^4A_2$, ${}^4E \leftarrow {}^4A_2$, ${}^4A_2(P) \leftarrow {}^4A_2$ and ${}^4E(P) \leftarrow {}^4A_2$ respectively. The four absorptions associated with compounds I, II correspond closely with those observed for [Co(trenMe)Br]-Br and suggest a similar stereochemistry at the cobalt centre. Solution spectra for compounds I and II in nitromethane are very similar to those observed in the solid state and indicate the presence of the species $[Co(NTBT)X]^+$ (X = Cl, Br) in both phases.

In the solid state, trigonal bipyramidal spectra are exhibited only by three other compounds (VI–VIII) and in these systems additional bands betray the presence of another cobalt(II) species with a different stereochemistry. Up to three bands can be assigned to trigonal bipyramidal transitions while the ${}^4A_2(P) \leftarrow {}^4A_2$ absorption appears to be hidden by very intense bands in the range 15300–16900 cm^{-1} (Cl) and 13700–16100 cm^{-1} (Br). These absorptions are assigned to the ν_3 manifold associated with tetrahedral anions. Other lower energy absorptions in the range 5000–7500 cm^{-1} are also assigned to ν_2 transitions in the same tetrahedral species.

Infrared evidence (see below) indicates the presence of one coordinated acetonitrile in compounds VI and VII. Since these compounds are prepared in acetonitrile and since the most labile site on the trigonal bipyramidal cation will be the axial site, not occupied by an NTBT donor atom, the most logical place to expect to find a coordinated acetonitrile would be at this axial site. While ligand field spectra are not inconsistent with such a species, other data suggest that acetonitrile is coordinated at the tetrahedral metal centre.

In the solid state, ligand field bands assigned to the trigonal bipyramidal cation in VI and VII are comparable with those observed for $[Co(NTBT)X]^+$ (X = Cl, Br) in compounds I, II, except for the ${}^4E \leftarrow {}^4A_2$ transitions which are slightly higher in energy, and support the presence of bound halogen. In solution the similarity is much more marked, although not all the trigonal bipyramidal bands could be observed. In the case of the complex $[Co(NTBT)Br_2]$-$CoBr_4] \cdot (MeNO_2)_2 \cdot 1.5EtOH$ (VIII) only two trigonal bipyramidal bands can be clearly seen and these correspond closely with those observed for compound II, both in the solid state and in solution.

Tetrahedral absorptions (ν_2) are found in the range 6500–7400 cm^{-1} (Cl) and 5700–6500 cm^{-1} (Br) in the solid state spectra of compounds VI and VII. Similar bands are also observed in nitromethane suggesting the same species both in solid state and in solution. These absorption energies are however somewhat higher than would be expected for tetrahalogenocobaltate(II) anions [12] and indicate a tetrahedral chromophore with a larger crystal field splitting. Addition of halide ion to nitromethane solutions of VI and VII causes dramatic changes in the ν_2 absorptions with major shifts to lower energy. The absorption envelope centred at 6700 cm^{-1} in the chloride complex increases in intensity and moves to lower energy with components at 6100, 5500 and 5300 cm^{-1}. In the case of the bromide complex the absorption envelope centred at 6500 cm^{-1} increases in intensity and shifts to lower energy. The highest energy component of this new absorption is observed at 5500 cm^{-1}. These observations are consistent with the presence of the species $[CoX_3(CH_3CN)]^-$ both in the solid state and in solution. Addition of halide ion simply produces the tetrahedral ions $[CoX_4]^{2-}$ (X = Cl, Br).

Although major changes were observed in the ν_2 bands the ν_3 envelope changes very little on addition of halide to solutions of VI and VII in nitromethane. Of major significance however is the fact that the trigonal bipyramidal bands are unaffected by addition of halide confirming the coordination of acetonitrile at the tetrahedral centres.

The complex $[Co(NTBT)Br]_2[CoBr_4] \cdot (MeNO_2)_2 \cdot 1.5EtOH$ (VIII) exhibits tetrahedral absorptions in its solid state spectrum in the range 5200–5500 cm^{-1} (ν_2) and 13700–15500 cm^{-1} (ν_3) which occur at lower energy than comparable bands observed for compounds VI and VII and are associated with the anion $[CoBr_4]^{2-}$. In solution in nitromethane a slight shift of these absorptions to higher energy is observed, consistent with the solvolysis of the tetrahedral anion. Addition of bromide ion to the solution causes shifts of ν_2 and ν_3 to lower energies, comparable with the solid state absorptions. The trigonal bipyramidal bands are not affected in energy by bromide addition but decrease in intensity on addition of excess bromide indicating decomplexation. The analogous chloro complex proved difficult to obtain in a pure state but displayed solid state absorptions indicative of the presence of the cation $[Co(NTBT)Cl]^+$ and the tetrahedral anion $[CoCl_4]^{2-}$. Compound VIII is analogous to the complexes $[Co(NTB)X]_2[CoX_4]$ (X = Cl, Br, NCS) obtained from the tris-benzimidazole tripod ligand NTB [6].

The remaining complexes (III–V, IX, X) exhibit solid state spectra which are typical of octahedral species. Two main absorptions are observed in the range 8000–9100 cm^{-1} and 17700–20000 cm^{-1} which are assigned to the ν_1 and ν_3 transitions in pseudo-octahedral cobalt(II) species. In some cases an additional weak band is observed in the range 15000–16000 cm^{-1}, which is tentatively assigned to ν_2. While in the case of other octahedral complexes (*e.g.* Ni(II)) low symmetry components of the ligand field are reflected in the splitting of bands, this is not normally the case for six-coordinate cobalt(II) systems. However intensity enhancement of the visible band is often observed. Complexes of the type $[Co(L)_2(NO_3)_2]$ (L = $(C_6H_5)_3PO$, $(CH_3)_3PO$, $(C_6H_5)_3AsO$), which have *cis*-octahedral structures [13, 14], have solution spectra in which visible (ν_3) molar absorption intensities fall in the range 100–200. Some splitting of ν_1 is observed for $[Co(L)_2(NO_3)_2]$, (L = $(C_6H_5)_3PO$, $(CH_3)_2PO$) [13]. In the case of the complexes $[Co(L)_2(NO_3)_2]$ (L = α-picoline, isoquinoline) fairly intense visible absorptions are observed ($\epsilon \simeq 150$) with some splitting of ν_3 and ν_1. These systems are assigned *cis*-octahedral structures involving bidentate nitrate groups [15].

In the solid state, splitting of ν_1 and ν_3 is observed for $[Co(NTBT)(H_2O)_2](ClO_4)_2$ (X). In solution however a marked splitting of both ν_1 and ν_3 is observed for both $[Co(NTBT)(NO_3)]NO_3 \cdot H_2O$ (IX) and $[Co(NTBT)(H_2O)_2](ClO_4)_2$ (X). In fact for compound X three components can be observed for ν_3. Splitting of these bands, coupled with the high intensity of ν_3 strongly supports *cis*-octahedral structures for these systems. In the case of compounds III and V their low solubility prevented running of suitable solution spectra. The complex $Co(NTBT)Br_2 \cdot (CH_3CN)_2$ (IV) has a solid state spectrum consistent with a six-coordinate derivative but in solution in nitromethane typical trigonal bipyramidal bands are observed. This system also has a molar conductance typical of a 1:1 electrolyte indicating the presence of the cation $[Co(NTBT)Br]^+$ in solution in nitromethane. Since infrared data indicate the presence of one coordinated acetonitrile (see below) a six-coordinate solid state species $[Co(NTBT)Br(CH_3CN)]^+$ is proposed.

A comparison of ligand field parameters for the octahedral complexes III–V, IX, X reveals that the highest values of Dq occur for systems in which oxygen or nitrogen donors occupy the fifth and sixth octahedral coordination sites, while the lowest value is observed for the complex $Co(NTBT)Cl_2 \cdot 2H_2O$. It seems clear that a CoN_4Cl_2 chromophore exists for this system, while in the case of the complex $Co(NTBT)Br_2 \cdot (CH_3CN)_2$, which has a substantially higher value of Dq, a coordinated acetonitrile seems quite likely.

Magnetism and Conductance

Four of the compounds assigned six-coordinate solid state structures on the basis of ligand field spectra (III–V, X) have magnetic moments (Table III) close to 5.0 BM or above, typical of octahedral derivatives. Low symmetry ligand field components in six-coordinate cobalt(II) systems can give rise to the splitting of T terms, which, if comparable with or greater than the spin–orbit coupling constant, can lead to magnetic moments approaching the spin-only value. In the case of the nitrato complex (IX), which has a somewhat lower magnetic moment, splitting of both ν_1 and ν_3 are observed in the solution electronic spectrum suggesting a low symmetry ligand field.

The slightly lower magnetic moments associated with the trigonal bipyramidal complexes (I, II) are typical of systems of this sort [6] while those observed for compounds VI, VII and VIII would seem reasonable for an average moment based on the presence of trigonal bipyramidal cations and tetrahedral anions.

Conductance data in nitromethane indicate the presence of 1:1 electrolytes for compounds I, II, IV, VI, VII and IX while the higher values associated with compounds VIII and X indicate the presence of 1:2 electrolytes.

Infrared Spectra

Single absorptions due to cobalt–halogen stretch are observed for compounds I and II (Table IV) consistent with the presence of trigonal bipyramidal cations. Absorptions due to acetonitrile are observed in the range 2240–2293 cm^{-1} and are consistent with lattice bound acetonitrile [9, 16]. Only one band attributable to cobalt–bromine stretch could be discovered in the infrared spectrum of $Co(NTBT)Br_2 \cdot (CH_3CN)_2$ (IV). Acetonitrile bands at 2250 and 2280 cm^{-1} can be associated with lattice bound acetonitrile but an absorption at 2310 cm^{-1} is consistent with coordinated acetonitrile [16]. Infrared evidence therefore suggests one coordinated

TABLE III. Magnetic Moment and Conductance Data.

Compound		Λ_M* (Ω^{-1} mol^{-1} cm^2)	μ(BM)†
I	$[Co(NTBT)Cl]BPh_4\cdot(CH_3CN)_2\cdot0.5H_2O$	48.0	4.65
II	$[Co(NTBT)Br]BPh_4\cdot(CH_3CN)_2$	53.3	4.41
III	$Co(NTBT)Cl_2\cdot2H_2O$	–	5.22
IV	$Co(NTBT)Br_2\cdot(CH_3CN)_2$	62.5	4.98
V	$[Co(NTBT)(NCS)_2]$	–	5.20
VI	$[Co(NTBT)Cl][CoCl_3(CH_3CN)]\cdot CH_3CN$	61.7	4.69
VII	$[Co(NTBT)Br][CoBr_3(CH_3CN)]\cdot CH_3CN$	62.5	4.71
VIII	$[Co(NTBT)Br]_2[CoBr_4]\cdot(MeNO_2)_2\cdot1.5EtOH$	141	4.80
IX	$[Co(NTBT)(NO_3)]NO_3\cdot H_2O$	74.4	4.70
X	$[Co(NTBT)(H_2O)_2](ClO_4)_2$	140	4.95

*Solvent nitromethane at approximately 10^{-3} *M* (25 °C).
†Magnetic moment measured in solid state by Faraday method (room temperature).

TABLE IV. Infrared Data (cm^{-1}).

Compound		ν(M–X)	Other bands
I	$[Co(NTBT)Cl]BPh_4\cdot(CH_3CN)_2\cdot0.5H_2O$	300	2240, 2250, 2280, 2293†
II	$[Co(NTBT)Br]BPh_4\cdot(CH_3CN)_2$	249	2240, 2250, 2280, 2290†
III	$Co(NTBT)Cl_2\cdot2H_2O$	250, 265(sh)	3480 (H_2O)
IV	$Co(NTBT)Br_2\cdot(CH_3CN)_2$	239	2250, 2280, 2310†
V	$[Co(NTBT)(NCS)_2]$		2043, 2065 (νCN, NCS) 255, 268 (νMN, NCS)
VI	$[Co(NTBT)Cl][CoCl_3(CH_3CN)]\cdot CH_3CN$	282,* 296, 317*	2260, 2290, 2318†
VII	$[Co(NTBT)Br][CoBr_3(CH_3CN)]\cdot CH_3CN$	220,* 245,* 253	2265, 2290, 2318†
VIII	$[Co(NTBT)Br]_2[CoBr_4]\cdot(MeNO_2)_2\cdot1.5EtOH$	234,* 258	3500 (EtOH), 1550, 650 ($MeNO_2$)
IX	$[Co(NTBT)(NO_3)]NO_3\cdot H_2O$		1722, 1758 ($\nu_1 + \nu_4$, bidentate NO_3) 804, 1483 (bidentate NO_3) 824, 1345 (NO_3^-) 3440 (H_2O)
X	$[Co(NTBT)(H_2O)_2](ClO_4)_2$		1095 (ν_3, ClO_4^-) 3460, 3540(sh) (coordinated H_2O)

*Cobalt–halogen stretching vibrations assigned to $[CoCl_3(CH_3CN)]^-$, $[CoBr_3(CH_3CN)]^-$, $[CoBr_4]^{2-}$.
†Absorptions due to lattice bound and coordinated acetonitrile.

bromine and one coordinated acetonitrile in the coordination sphere in compound IV.

The complex $Co(NTBT)Cl_2\cdot2H_2O$ (III) has no infrared absorption around 300 cm^{-1}, where one might expect to find terminal cobalt–chlorine stretch. The highest energy absorptions which could be associated with cobalt–chlorine stretching occur around 250 cm^{-1}, more typical of chloro-bridged species. No evidence exists in the ligand field or infrared spectra of this system to suggest the presence of coordinated water and so a chlorine bridged system is proposed involving a dimeric species $[Co_2(NTBT)_2Cl_2]Cl_2\cdot4H_2O$.

Compounds VI and VII have rather complex absorptions associated with cobalt–halogen stretch. Bands at 296 cm^{-1} (Cl) and 252 cm^{-1} (Br) are assigned to cobalt–halogen stretch in the trigonal bipyramidal cations $[Co(NTBT)X]^+$ while the other bands are assigned to the anions $[CoX_3(CH_3CN)]^-$ (Table IV). Lowering the symmetry of the tetrahedral species $[CoX_4]^{2-}$ to C_{3v} splits the ν_3 absorption into two bands. In other systems of the sort $[LCoX_3]^-$ [L = Ph_3P, Py, α-picoline; X = Cl, Br) two cobalt–halogen vibrations are observed in the range 282–320 cm^{-1} (Cl) and 210–252 cm^{-1} (Br) [17, 18]. The presence of coordinated acetonitrile in VI and VII is confirmed by absorptions at 2318 cm^{-1}, while other absorptions indicate the presence of lattice bound acetonitrile also. Compound VIII has two bands associated with cobalt–bromine stretch. An absorption at 258 cm^{-1} can be assigned to the trigonal bipyramidal cation $[Co(NTBT)Br]^+$, while the absorption at 234 cm^{-1} is consistent with the presence of the tetrahedral anion $[CoBr_4]^{2-}$ [19].

The thiocyanate complex $[Co(NTBT)(NCS)_2]$ (V) has two absorptions due to C–N stretching at 2043 and 2065 cm^{-1} and two bands in the far infrared (255, 268 cm^{-1}) which can be associated with cobalt–nitrogen stretching. Two pairs of bands of this sort are indicative of a *cis* arrangement of nitrogen bound thiocyanate groups consistent with a *cis* six-coordinate structure $[Co(NTBT)NCS)_2]$.

The complex $[Co(NTBT)(NO_3)]NO_3 \cdot H_2O$ (IX), exhibits only two major nitrate combination bands ($\nu_1 + \nu_4$) at 1722 and 1758 cm^{-1}. A separation of 36 cm^{-1} is considered too big to be associated with monodentate nitrate and so these absorptions are assigned to a bidentate nitrato group [20]. Since this complex contains two nitrate groups it is surprising that only two combination bands are observed; a third absorption due to ionic nitrate would be anticipated. While nitrate fundamentals are often difficult to pick out in coordination complexes due to interfering ligand absorptions, it is possible in this case to assign fundamental vibrations associated with both ionic and bidentate nitrate (Table IV). The combination band due to ionic nitrate, which would be expected to occur around 1750 cm^{-1}, may well be part of the rather broad asymmetric absorption observed at 1758 cm^{-1}. In another example, the copper nitrate complex $[Cu(NTBT)(NO_3)]NO_3 \cdot 0.5H_2O$, which was shown to have a distorted trigonal bipyramidal structure, gave a very weak combination band associated with ionic nitrate, which could only be observed by using very strong mulls and ordinate expansion. The perchlorate complex (X) contains coordinated water, according to infrared data, and ionic perchlorate.

Conclusion

Although trigonal bipyramidal systems of the type $[Co(NTBT)X]^+$ have been synthesized (X = Cl, Br), *cis*-octahedral species appear to be more common. This is in direct contrast to the situation that exists for cobalt(II) complexes of the analogous 'tripod' ligand tris-(2-benzimidazolylmethyl)amine (NTB), where only trigonal bipyramidal species were produced [6]. The crystal field strength of the two ligands NTB and NTBT appears to be comparable and in terms of steric bulk of the donor groups the difference between benzothiazole and benzimidazole would perhaps be considered small. One difference however involves the presence of the imidazole NH in NTB which has been shown to be a hydrogen bonding site in its cobalt complexes [6]. The presence of hydrogen bonded donor groups around the periphery of the three equatorial benzimidazole groups in cobalt complexes of NTB could provide the extra steric bulk necessary to form five-coordinate systems only. Such a situation could not, of course, exist in complexes of NTBT.

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