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Distorted Five-Coordinate Cobalt(II). The Structure of Bromotris(3-aminopropyl)aminecobalt(II) Bromide Hemiethanolate

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Received November 16, 1970

The structure of bromotris(3-aminopropyl)aminecobalt(II) bromide hemiethanolate, $[Co(trpn)Br]Br \cdot 0.5C_2H_5OH$, has been determined from three-dimensional X-ray data collected by counter methods. The final R factor on F for 578 F^2 values above $\sigma(F^2)$ is 6.5%. The material crystallizes with six formula units per cell in space group $D_{3d}{}^5$-$R\bar{3}m$ of the trigonal system in a cell of dimensions a = 8.6261 (13) and c = 38.900 (7) Å. Calculated and measured densities are 1.71 and 1.70 g cm^{-3}, respectively. The site symmetry at Co is $3m$ (C_{3v}) thus implying a statistical disorder between the two enantiomorphic forms of the asymmetric complex cation. The structure consists of discrete $Co(trpn)Br^+$ cations in a relatively open lattice array. Ethanol solvent molecules are trapped in this crystal array and are 12-fold disordered about the special position 3(b). The $Co(trpn)Br^+$ cation has a trigonal-bipyramidal structure with axial and equatorial Co–N bond lengths of 2.194 (9) and 2.055 (10) Å, respectively, with an N_{ax}–Co–N_{eq} angle of 91.1 (3)°. The unusually long Co–Br bond length of 2.658 (3) Å is compared with that for $[Co(N(CH_2CH_2N(CH_3)_2)_3)Br]Br$ of 2.431 (4) Å and cited as evidence for distortion toward a four-coordinate geometry.

Introduction

Complexes of the tripod tetramine ligand tris(2-aminoethyl)amine, $N(CH_2CH_2NH_2)_3$, here abbreviated as tren, have been known since 1925.[1] Although originally thought to form tetrahedral complexes[2,3] the ligand is now known to form either six-coordinate complexes such as $Ni(tren)(NCS)_2$[4] or five-coordinate complexes such as [Cu(tren)(NCS)][SCN],[5] [Zn(tren)(NCS)][SCN],[6] and [Co(tren)(NCS)][SCN].[7] More recently, complexes of the sterically hindered derivative Me_6tren, $N(CH_2CH_2N(CH_3)_2)_3$, have been prepared for almost the entire first row of transition elements.[8-10] X-Ray analysis for the isomorphous series [M(Me_6tren)Br]Br (M = Mn → Zn) have shown the complexes to be trigonal-bipyramidal cations with one free Br^- anion.[11-13] The addition of another CH_2 group in the ethylene bridging chains of tren produces a more facultative[14] ligand whose structure potentially allows formation of tetrahedral complexes. This ligand, $N(CH_2CH_2CH_2NH_2)_3$, "trpn," has been little studied since first prepared.[15] Thermochemical and spectroscopic studies[16,17] of aqueous solutions of M^{2+} complexes of trpn have indicated that Co^{2+} and Cu^{2+} are five-coordinate, Ni^{2+} is octahedral, and Zn^{2+} is tetrahedral.

Interrante and Shafer[18,19] have reported the preparation and properties of some high-spin complexes of Co(II) with trpn and some Schiff base derivatives. Magnetic and spectroscopic studies were made of the complexes $Co(trpn)X_2$ (X = Br, I, ClO_4, NCS, $B(C_6H_5)_4$) and $[Co(trpn)X][B(C_6H_5)_4]$ (X = Cl, Br, ClO_4). Of these, $Co(trpn)(NCS)_2$ is assigned a six-coordinate, $[Co(trpn)Br][B(C_6H_5)_4]$ a five-coordinate, and $[Co(trpn)][B(C_6H_5)_4]_2$ a four-coordinate geometry. The visible reflectance spectra of [Co(trpn)Br]Br and $[Co(trpn)(ClO_4)][ClO_4]$ are very similar to that of $[Co(trpn)][B(C_6H_5)_4]_2$ and slightly different from that of $[Co(trpn)Br][B(C_6H_5)_4]$ (which in turn is almost the same as $Co(Me_6tren)Br^+$, known[12] to be five-coordinate). Since the complex [Co(trpn)Br]Br seemed to exhibit properties between those of the four- and five-coordinate complexes, a structural study was undertaken to establish the geometry of this complex and the series.

Experimental Section

Data Collection.—The complex [Co(trpn)Br]Br was prepared as previously described.[18] Well-formed purple crystals were obtained by cooling to 30° over a period of approximately 50 hr an ethanol solution originally saturated at 65°. The crystals so obtained are of two distinct crystalline habits: tetragonal needles (the predominant form) and trigonal plates. Several crystals of each type were sealed within thin-walled glass capillaries. All of the operations described were carried out under a carefully purified nitrogen atmosphere in an inert-atmosphere box.

A series of precession photographs (Mo Kα radiation) of the tetragonal needles exhibited $4/mmm$ Laue symmetry (a = 11.6, c = 11.1 Å) with no apparent systematic absences. A satisfactory choice of space group could not be made consistent with the observed density of 1.76 g/cm^3 (flotation in CCl_4–$CHBr_3$ solutions) and so further studies were carried out on the trigonal plates. These exhibit a Laue symmetry of $\bar{3}m$ with systematic absences hkl, $-h + k + l \neq 3n$. The space group $R\bar{3}m$ and its subgroups $R32$ and $R3m$ are consistent with these observations. Unit cell parameters and the crystal orientation were determined by a least-squares fit to the setting angles of 10 reflections carefully centered on an automatic Picker four-circle diffractometer.[20] These angles were measured with the same instrument settings later used in intensity measurement. The cell parameters (Mo Kα, λ 0.70926 Å) at 22° are a = 8.6261 (13) and c = 38.900 (7) Å. The density observed by flotation in CCl_4–$CHBr_3$ solutions is 1.70 (1) g/cm^3. The density calculated for six formula units per cell of $[Co(trpn)Br]Br \cdot 0.5C_2H_5OH$ is 1.71 g/cm^3.

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(20) The diffractometer is automated by a PDP8/I computer with 4 K memory. Except for minor modifications, the controlling programs are those of Busing and Levy as modified by Picker Corp.

The data crystal was a truncated trigonal plate, 0.20 mm thick and of cross section 0.36 × 0.26 mm. It was mounted with an arbitrary orientation on a eucentric goniometer head in order to minimize multiple diffraction effects.[21] The pulse height analyzer was set to admit 90% of maximum intensity at full window width and was centered on the Mo Kα energy. Attenuators were used such that the count rate never exceeded 10,000 cps. The detector was placed 33 cm from the crystal with a receiving aperture 7 × 7 mm. A highly oriented graphite monochromator ($2\theta_m = 12.02°$) was used with a takeoff angle of 1.7°. At this angle the height of a selected peak was about 85% of its maximum value as a function of takeoff angle.

Data were collected by the θ–2θ scan technique[22] at a scan rate of 1.0°/min. The scan was from 0.55° below the calculated Kα_1 peak to 0.55° above the Kα_2 peak. A 10-sec background count was recorded before and at the end of each scan. Two symmetry-related forms, hkl and $kh\bar{l}$, were collected out to a Bragg 2θ angle of 60°. Three standard reflections (600, 060, and 0,0,30) were monitored during data collection. There was a uniform drop in these counts during the experiment of 1.5%. The data were extensively checked for errors[22] and reduced to values of F^2 after correcting for Lorentz and polarization effects.[23] Standard deviations were assigned according to the formula

$$\sigma(I) = [CT + 9 + {}^1/_4(t_c/t_b)^2(B_1 + B_2 + 18) + (pI)^2]^{1/2}$$

where CT is the total integrated peak count obtained in a scan time of t_c, B_1 and B_2 are the background counts each obtained in the time t_b, and $I = CT + 4.5 - 0.5(t_c/t_b)(B_1 + B_2 + 9)$. The appearance of the constants 4.5, 9, and 18 is due to the statistical effect of dropping the last decimal place when recording the total count in the scaler.[22] Our data processing program multiplies all counts by 10 to bring them back to their true values but the truncation results in systematically lower counts than actually observed if a correction is not applied.[23] A value of 0.04 was assigned to the parameter p in order to avoid overweighting strong reflections in the refinement. A total of 1945 reflections were observed. Of these, 1289 had $F^2 > \sigma(F^2)$ and 876 had $F^2 > 3\sigma(F^2)$.

After careful measurement of the crystal with a microscope and micrometer eyepiece, an absorption correction was applied. For a linear absorption coefficient of 61.1 cm^{-1} the transmission factors range from 0.32 to 0.38. The two equivalent forms were averaged with an agreement factor for averaging of 3.6% based on F^2 and a predicted weighted R factor on F^2 of 10.0%. A total of 970 independent reflections resulted from the averaging of which 578 gave $F^2 > \sigma(F^2)$. The latter set was used in subsequent refinements.

Solution and Refinement of the Structure.—A three-dimensional Patterson map[23] showed all large peaks along the threefold axis, consistent with the site symmetry requirements. Trial positions for the bromine and cobalt atoms and for the axial nitrogen atom were determined from the Patterson map. This solution was consistent with either of the space groups $R32$ or $R\bar{3}m$. Least-squares and difference Fourier techniques gave the remaining atom positions plus their mirror-related positions. In this and subsequent calculations the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where F_o and F_c are the observed and calculated structure factors, respectively. The weights, w, were taken as $4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factors for neutral Br, Co, O, N, and C were calculated from the values tabulated by Cromer and Mann.[24] The neutral hydrogen scattering factors were those of Stewart, *et al.*,[25] The effects of anomalous dispersion were included in F_c using the values of f' and f'' for Br and Co calculated by Cromer.[26] Refinements in $R32$ (where the molecule is ordered with C_3 site symmetry) were about as successful as in $R\bar{3}m$ (where the $-CH_2CH_2CH_2NH_2$ arms of the ligand are disordered since the molecule has C_{3v} site symmetry). Two of the carbon atoms in the model are very close to the mirror plane. Thus over 80% of the electron density lies either on the mirror plane or very near to it. Nevertheless a choice could be made between a centrosymmetric and noncentrosymmetric space group based on intensity considerations. A search of the structure factor list when the structure was near final refinement gave a set of centrosymmetrically related structure factors whose calculated magnitudes differed by large amounts. These differences range from 7 to 4 times the assigned standard deviations and so should be easily distinguishable. Scan data were carefully measured for this set of reflections and the observed values are compared (in Table I) with those calculated for a noncentrosymmetric structure. It is clear from this comparison that the structure is centrosymmetric and the space group is then $R\bar{3}m$. The primary amine groups and the aliphatic bridging chains are disordered about the vertical mirror plane. Since two of the carbon atoms in each chain lie within 0.3 Å of the mirror plane, convergence of least-squares refinements was very slow due to the near singularity of the model. This singularity is easily removed by treating the three-atom cluster N–C–C as a rigid group with a fixed N–C–C bond angle. Hydrogen atoms were included in the model but their positional and thermal parameters were not refined. Their positions were calculated assuming tetrahedral geometry about C and N with C–H and N–H bond lengths of 1.0 Å in order partially to account for the apparent contraction of such bond lengths from X-ray diffraction data. Introduction of the hydrogen atoms gave a significant improvement in the agreement factors.

TABLE I

OBSERVED AND CALCULATED VALUES OF F^2 FOR SELECTED REFLECTIONS IN SPACE GROUP $R32$

h	k	l	F_o^2 [a]	F_c^2	h	k	l	F_o^2 [a]	F_c^2
$\bar{2}$	$\bar{1}$	$\bar{4}$	291	342	$\bar{3}$	$\bar{1}$	$\overline{14}$	55	103
2	1	4	305	259	3	1	14	43	55
$\bar{1}$	$\bar{3}$	$\bar{4}$	80	237	$\bar{1}$	$\bar{4}$	$\bar{3}$	391	458
1	3	4	59	79	1	4	3	355	377

[a] These values were measured for a different crystal than that used in the collection of intensity data. They are not corrected for absorption and so differ somewhat in absolute and relative magnitude from the values of F^2 used in least-squares refinement.

Difference Fourier maps at this stage of the refinement showed peaks as large as 1.5 e$^-$/Å^3. These peaks were located around Br$_1$ and Br$_2$ and at a large hole in the structure at 0,0,$^1/_2$. Around the bromine atoms were tetrahedra of peaks and troughs which indicated either some disorder (with these atoms located slightly off the threefold axis) or a complex and large anisotropic vibrational motion resulting from a potential field with threefold symmetry. To account for this the bromine atoms were placed slightly off the threefold axis in a series of refinements. The weighted R factor, R_2, dropped by 3% where the standard and weighted agreement factors, R_1 and R_2, are defined as

$$R_1 = \frac{\sum||F_o| - |F_c||}{\sum|F_o|} \quad R_2 = \left(\frac{\sum w(|F_o| - |F_c|)^2}{\sum wF_o^2}\right)^{1/2}$$

The peak at 0,0,$^1/_2$ is due to one ethanol of crystallization which is disordered about a position of $\bar{3}m$ symmetry. Since the ethanol is spread out over 12 symmetry-related positions within this cavity, the proper choice for its position is not obvious and least-squares refinement of its position is not appropriate. This difficulty was solved by choosing carefully the best set of atom positions and introducing the ethanol into the model as a fixed, rigid group at this position. The refinement then converged to give 6.49 and 6.52% for R_1 and R_2, respectively. The highest peak in a final difference Fourier map was 0.5 e$^-$/Å^3 or about 10% of the axial nitrogen peak in this structure. The final value for the error in an observation of unit weight, defined as

$$\left(\frac{\sum(|F_o| - |F_c|)^2/\sigma^2(F_o)}{N_o - N_v}\right)^{1/2}$$

is 1.67 where N_o and N_v are the number of observations and variables, respectively. A comparison of F_o and F_c showed no

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[23] In addition to various local programs for the CDC 6400 computer, local modifications of the following programs were employed: Hamilton's GONO9 absorption program, Zalkin's FORDAP Fourier program, the Doeden–Ibers group least-squares program NUCLS (based on the Busing–Levy program ORFLS), the Busing–Levy program ORFFE, and Johnson's thermal ellipsoid program ORTEP. We express our appreciation to J. A. Ibers for copies of several of his programs.

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TABLE II

POSITIONAL AND THERMAL PARAMETERS FOR $[Co(trpn)Br]Br\cdot 0.5C_2H_5OH$

Atom	10^4x	10^4y	10^5z	$10^4\beta_{11}$[a]	$10^4\beta_{22}$	$10^5\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Br_1	$-y$	−133 (30)	16,150 (5)	β_{22}	345 (16)	47 (1)	46 (23)	0 (2)	$-\beta_{13}$
Br_2	$-y$	170 (18)	40,030 (6)	β_{22}	258 (19)	84 (1)	42 (11)	8 (2)	$-\beta_{13}$
Co	0	0	22,963 (4)	β_{22}	186 (3)	55 (1)	$^1/_2\beta_{22}$	0	0
N_1	0	0	28,603 (33)	β_{22}	143 (12)	43 (6)	$^1/_2\beta_{22}$	0	0
Cl	−1454 (13)	220 (13)	30,065 (21)	206 (24)	251 (26)	57 (6)	129 (22)	6 (3)	4 (3)

Group[b]	10^4x_g	10^4y_g	10^5z_g	δ	ϵ	η	B_{N_2}[c]	B_{C_3}	B_{C_2}
$N_2C_3C_2$	−1878 (16)	1919 (24)	25,019 (18)	1.195 (33)	2.174 (6)	−1.556 (18)	6.4 (2)	8.1 (3)	5.2 (3)

[a] The form of the thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] x_g, y_g, and z_g are the fractional coordinates of the group origin. The angles δ, ϵ, and η (in radians) have been described by R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965). [c] Isotropic temperature factor in square ångströms.

evidence of secondary extinction effects.[27] None of those reflections for which $F^2 < \sigma(F^2)$ gave $|F_o^2 - F_c^2| > 2.5\sigma(F_o^2)$. The final values of the atomic and group parameters along with their standard deviations estimated from the inverse matrix are given in Tables II and III. Table IV lists the fixed hydrogen and ethanol atom positions used in the calculations. Table V lists the important bond distances and angles, and Table VI lists the rms amplitudes of vibration of the nonhydrogen atoms.

TABLE III

POSITIONAL AND THERMAL PARAMETERS OF GROUP ATOMS

Group atoms	x	y	z	B, Å^2
N_2	−0.0350 (13)[a]	0.2188 (13)	0.2286 (2)	6.4 (2)
C_3	−0.1878 (16)	0.1919 (24)	0.2502 (2)	8.1 (3)
C_2	−0.1381 (16)	0.1988 (18)	0.2884 (2)	5.2 (3)

[a] The fixed group parameters are the distances C–C = 1.54 Å and C–N = 1.48 Å and the angle C–C–N = 109.5°.

TABLE IV

CALCULATED POSITIONS OF HYDROGEN AND ETHANOL ATOMS

	x	y	z	B,[a] Å^2
H_1N_2	0.076	0.325	0.237	7.0
H_2N_2	−0.057	0.241	0.204	7.0
H_1C_1	−0.136	0.024	0.326	5.0
H_2C_1	−0.263	−0.082	0.293	5.0
H_1C_2	−0.014	0.301	0.292	6.0
H_2C_2	−0.224	0.218	0.303	6.0
H_1C_3	−0.299	0.072	0.250	8.5
H_2C_3	−0.221	0.287	0.250	8.5
C_1	−0.072	0.010	0.511	10
C_2	0.084	−0.014	0.498	10
O_x	0.015	−0.166	0.475	10

[a] The thermal parameters assigned to the hydrogen atoms were chosen as approximately $B_A + 1$, where B_A is the isotropic thermal parameter for the atom to which the hydrogen is bound.

Discussion of the Structure

The crystal consists of discrete $Co(trpn)Br^+$ cations (Figure 1) and Br^- ions, arranged in layers in the xy plane as diagrammed in Figure 2. The cobalt atom is coordinated by the four amine nitrogen atoms and by one bromide ion. The crystallographic threefold axis passes through the axial nitrogen, cobalt, and bromine atoms as well as the bromide anion. Although the basic geometry is the same as that reported for $[Co(Me_6tren)Br]Br$,[12] there are some notable differences which indicate changes in the coordination and explain the observed difference in visible spectra. The geometries of the two complexes are compared in Table VII. The most obvious and important difference

TABLE V

BOND LENGTHS AND ANGLES IN $[Co(trpn)Br]Br\cdot 0.5C_2H_5OH$

Bond	Distance, Å	Atoms	Angle, deg
$Co-N_1$(ax)	2.194 (9)	Br_1-Co-N_1	175.7 (3)
$Co-N_2$(eq)	2.055 (10)	N_1-Co-N_2	91.1 (3)
Difference	0.139 (14)	$Co-N_1-C_1$	112.7 (5)
Co–Br	2.658 (3)	$N_1-C_1-C_2$	112.7 (8)
N_1-C_1	1.473 (10)	$C_1-C_2-C_3$	112.4 (9)
C_1-C_2	1.569 (15)	$C_2-C_3-N_2$	109.5[a]
C_2-C_3	1.540[a]	C_3-N_2-Co	111.9 (8)
C_3-N_2	1.480[a]		

[a] Fixed parameter in the group refinement.

TABLE VI

RMS AMPLITUDES (Å) OF VIBRATION ALONG PRINCIPAL THERMAL ELLIPSOID AXES

Atom	Axis 1	Axis 2	Axis 3
Br_1	0.189 (2)	0.312 (7)	0.312 (7)
Br_2	0.210 (5)	0.270 (10)	0.306 (9)
Co	0.205 (2)	0.229 (2)	0.229 (2)
N_1	0.181 (13)	0.201 (9)	0.201 (9)
Cl	0.196 (12)	0.238 (14)	0.269 (14)

TABLE VII

COMPARISON OF BOND LENGTHS AND ANGLES FOR $Co(trpn)Br^+$ and $Co(Me_6tren)Br^+$

	$Co(trpn)Br^+$	$Co(Me_6tren)Br^+$[a]
Co–Br, Å	2.658 (3)	2.431 (4)
$Co-N_{ax}$, Å	2.19 (1)	2.15 (2)
$Co-N_{eq}$, Å	2.06 (1)	2.08 (2)
$Br-N_{eq}$, Å	3.33 (2)[b]	3.44 (2)
$N_{ax}-CO-N_{eq}$, deg	91.1 (3)	81.1 (8)

[a] Reference 12. [b] Average value for nonbonded distance.

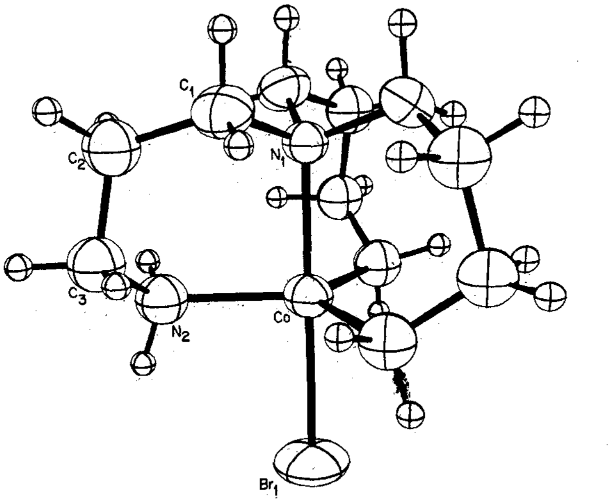

Figure 1.—A perspective drawing of the $Co(trpn)Br^+$ cation. The isotropic thermal parameters used for the group and hydrogen atoms were chosen as 4.5 and 1.0 Å^2, respectively, for visual clarity.

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[27] A listing of structure factor amplitudes will appear immediately following this article in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth Street, N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit $3.00 for photocopy or $2.00 for microfiche.

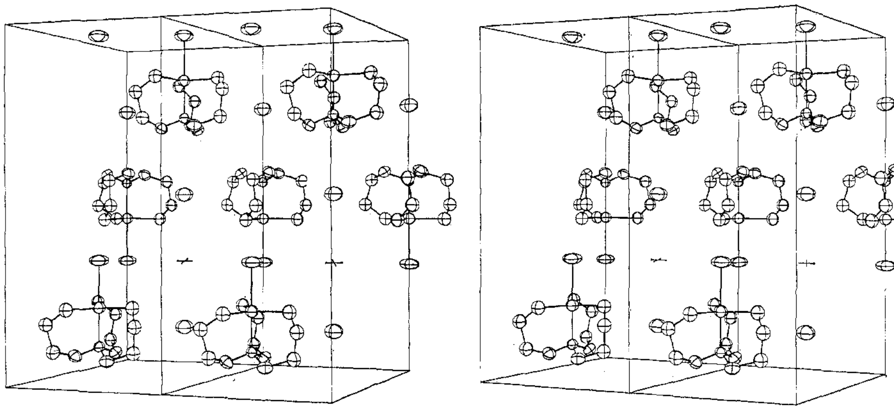

Figure 2.—Packing diagram of [Co(trpn)Br]Br · $0.5C_2H_5OH$ (stereoscopic view). The horizontal axis is *b* and the vertical is *c*. The width of the diagram is two unit cells, the height is a half cell. The ethanol molecules are disordered about the positions marked with an × in the diagram.

is between the Co–Br bond lengths of 2.658 (3) and 2.431 (4) Å for [Co(trpn)Br]Br and [Co(Me_6tren)Br]Br, respectively. The longer distance found here is closer to those found in $CoBr_2 \cdot 2H_2O$.[28] In that structure the cobalt is octahedrally coordinated by bridging bromine atoms with Co–Br bond lengths of 2.603 and 2.641 Å. The sum of the Pauling radii for octahedral Co(II) and Br^- is 2.43 Å.[29] These comparisons emphasize the unusually weak Co–Br bond that is present in [Co(trpn)Br]Br. The lengthening of the Co–Br bond is sufficient to regard this complex as an intermediate or transition geometry between the five-coordinate structure found in [Co(Me_6tren)Br]Br and a four-coordinate tetrahedral structure in which the four trpn nitrogen atoms occupy the coordination sites. An explanation for this behavior can be found in the nonbonding interaction between Br_1 and N_2. The sum of the van der Waals radii for these atoms is 3.45 Å. The average Br_1–N_2 nonbonded distance is 3.33 Å. This distance in [Co(Me_6tren)Br]Br is 3.44 (2) Å. There is strong interatomic repulsion between Br_1 and N_2, and as the Co–Br bond lengthens due to this repulsion, one might expect the cobalt to move up out of the plane formed by the equatorial nitrogen atoms in order to move toward a tetrahedral geometry. However, if the N_1–Co–N_2 angle were larger in the present structure and the N–Br nonbonded contact stayed approximately constant, the Co–Br bond length would increase to such an extent that the bromine atom would probably completely leave, resulting in a four-coordinate complex. Sacconi, *et al.*, have made a similar observation in the complex Ni(tda)I^+ [30] (tda = $N(CH_2CH_2P(C_6H_5)_2)_3$), where the Ni–I bond is unusually long, apparently due to short P–I nonbonding contacts. The opposite distortion occurs for the cobalt complex Co(tda)Cl^+,[31] where the metal is well below the plane formed by the equatorial ligands and the Co–N bond, 2.675 (10) Å, is very long.

The equatorial Co–N bond of 2.06 (1) Å is approximately the same as that found in the Me_6tren complex. The axial Co–N bond of 2.19 (1) Å may be significantly longer than that of 2.15 (2) Å for [Co(Me_6tren)Br]B- but is yet comparable. The differences between axial and equatorial bond lengths are 0.13 and 0.07 Å for the two complexes. This is consistent with the difference of 0.123 (9) Å reported for the monodentate complex Co(2-picoline *N*-oxide)$_5{}^{2+}$.[32] Contraction and expansion of axial *vs.* equatorial metal–ligand bond lengths for trigonal-bipyramidal complexes have been observed and qualitatively explained previously,[11,33,34] and recently one system has been treated quantitatively.[35] There are two main factors involved. The first of these is a ligand–ligand repulsion phenomenon which favors axial elongation since, for whatever force field is chosen, the axial ligands encounter greater ligand–ligand interactions than the equatorial when these metal–ligand bond lengths are equal. The second factor is the distribution of the electrons in the metal d orbitals. This creates steric effects which can either counter or reinforce the ligand repulsion effect. In trigonal-bipyramidal high-spin Co(II) the d electrons have relatively little stereochemical effect since there is a uniform distribution in the σ antibonding orbitals $d_{x^2-y^2}$, d_{xy}, and d_{z^2}. As a result there is a net elongation of the axial bond lengths in this structure, caused by ligand repulsion.

The N_1–Co–N_2 angle of 91.1 (3)° is much larger than that for the Me_6tren complex. The increase of 10° is the expected increase for expansion from a five-membered to a six-membered chelate ring.[21,36,37] Both C_2 and C_3 lie close to the mirror plane such that the atom positions and their mirror images can be connected to make chair or boat conformers, where in both cases chemically reasonable bond lengths and angles result. A boat conformer should be energetically quite unfavorable in this complex and so the chair conformer was used throughout the structure analysis.

There is no evidence of hydrogen bonding between the bromine atoms and amine protons. Except for the ethanol of crystallization, there is no nonhydrogen atom less than 3.7 Å from Br_2.

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Acknowledgments.—We gratefully acknowledge support of this research by the National Science Foundation through Grant GP-13278. We thank the University of California Computer Center for the computing time used in this work and the National Institutes of Health for a predoctoral fellowship to J. L. S.

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The Effects of the Nature of the Counteranion on the Structure of 1,1,7,7-Tetraethyldiethylenetriamine- and Diethylenetriaminecobalt(II), -nickel(II), and -copper(II) Pseudohalide Complexes[1]

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Received August 24, 1970

The occurrence of stable, square-planar, N-bonded complexes of the type $[M(Et_4dien)NCX][B(C_6H_5)_4]$ (M = Ni(II), Cu(II); X = O, S, Se; Et_4dien = 1,1,7,7-tetraethyldiethylenetriamine) is contrasted with the N→X-bonded reisomerizations which have been observed for $[Pd(Et_4dien)NCX][B(C_6H_5)_4]$ (X = S, Se) complexes in the solid state. The latter reestablishes a soft–soft interaction, whereas, in the former case, a preferential hard–hard interaction would be destroyed. The nickel(II) cyanate and thiocyanate complexes were found to be thermochromic. The corresponding Co(II) complexes could not be prepared; instead, five-coordinate complexes of the type $Co(Et_4dien)(NCX)_2$ (X = O, S, Se) are formed. The corresponding Ni(II) complexes, $Ni(Et_4dien)(NCX)_2$ (X = O, S, Se), exhibit a variety of geometries: the cyanate is five-coordinate, both in the solid state and in acetonitrile solution; the thiocyanate is dimeric in the solid state, with bridging thiocyanates creating an octahedral environment, but exists as an equilibrium mixture of four- and five-coordinate species in acetonitrile solution, and the selenocyanate is four-coordinate in the solid state and primarily so in acetonitrile solution. The diethylenetriamine complexes $[Cu(dien)NCS]NCS$, $[Cu(dien)NCO][B(C_6H_5)_4]$, and $[M(dien)_2](NCSe)_2$ (M = Co, Ni) were also prepared. The structural conclusions are based on the results of molar conductance and infrared and electronic spectral data.

Introduction

Among the several factors[2] which determine the bonding modes adopted by ambidentate ligands in coordination complexes, counterion control was undoubtedly the least anticipated. Control by both counteranions,[3] *e.g.*, $[Pd(Et_4dien)NCS]SCN$ *vs.* $[Pd(Et_4dien)SCN][B(C_6H_5)_4]$ (Et_4dien = 1,1,7,7-tetraethyldiethylenetriamine), and countercations,[4] *e.g.*, $K_3[Co(CN)_5SCN]$ *vs.* $[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5NCS]$, has been demonstrated. Likewise, $Pd(Et_4dien)SeCN^+$ isomerizes to the N-bonded isomer in solution but reisomerizes to the Se-bonded isomer in the solid state following its isolation as the tetraphenylborate salt.[3] The selenocyanate ion also displays[5] a different bonding preference in the complexes $K_3[Co(CN)_5SeCN]$ and $[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5NCSe]$. The counteranion control has been attributed[3] to steric effects in the solid state since $[Pd(Et_4dien)NCO][B(C_6H_5)_4]$, with a smaller exo atom in the cation, does not isomerize,[6] whereas the countercation control has been attributed[4] to preferential hard–hard and soft–soft interactions in the solid state. In addition to the effects of changing the ambidentate group, our exploration of the limitations of counterion control has involved a study of the effects of changing the metal coordination center. We now wish to report the results of this study involving Et_4dien and diethylenetriamine (dien) pseudohalide complexes of cobalt(II), nickel(II), and copper(II).

Experimental Section

Preparation of Complexes.—$M(Et_4dien)Cl_2$[7] (M = Co, Ni), $Ni(dien)_2Cl_2$,[8] $Cu(dien)Cl_2$,[8] and $Co(Et_4dien)(NCS)_2$[9] were prepared according to literature methods.

$[M(Et_4dien)(NCO)_2]$ Complexes.—Sodium cyanate (1.3 g, 0.02 mol) and the appropriate anhydrous metal(II) halide (0.01 mol) were stirred in 100 ml of anhydrous methanol, whereupon 3.0 g (0.02 mol) of silver cyanate was added, and the stirring continued for an additional period. The precipitated silver halide was removed by filtration, and 6 ml (0.033 mol) of Et_4dien was added to the filtrate. After standing overnight, the solution was again filtered. Cooling the filtrate to −15° yielded the crystalline product, which was isolated by filtration, washed, and dried *in vacuo*. Details of preparation are as follows: for M = Co(II), 1.3 g of $CoCl_2$, stirring periods of 5 and 10 min, violet crystals washed with ethanol and ether; for M = Ni(II), 2.2 g of $NiBr_2$, stirring periods of 5 and 0.5 hr, green crystals washed with a little cold methanol, changing color to yellow on drying.

$[M(Et_4dien)(NCX)_2]$ (X = S, Se) Complexes.—Alcoholic solutions of the appropriate potassium or sodium pseudohalide and hydrated metal(II) nitrate were mixed and the precipitated potassium or sodium nitrate removed by filtration. After adding Et_4dien to the filtrate, the resulting solution was stirred, cooled, or reduced in volume to yield the crystalline product, which was isolated by filtration. Details of preparation are as follows: for M = Ni(II) and X = S (dimeric in solid state, *vide infra*), 2.0 g (0.02 mol) of KNCS in 50 ml of ethanol (at boiling point prior to mixing), 2.9 g (0.01 mol) of $Ni(NO_3)_2 \cdot 6H_2O$ in 25 ml of ethanol, 2.2 g (0.01 mol) of Et_4dien, solution allowed to stand overnight, green crystals washed with ethanol and dried *in vacuo;* for M = Cu(II) and X = S, 2.0 g (0.02 mol) of KNCS in 50 ml of methanol, 2.4 g (0.01 mol) of $Cu(NO_3)_2 \cdot 3H_2O$ in 50 ml of methanol, 2.2 g (0.01 mol) of Et_4dien in 25 ml of methanol, solution evaporated to 75 ml under reduced pressure, blue crystals re-

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[1] Presented at the Fifth Middle Atlantic Regional Meeting of the American Chemical Society, Newark, Del., April 1–3, 1970; see Abstracts, p 47; abstracted in part from the Ph.D. dissertation of T. P. O., University of Delaware, June 1969.

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