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## Ligand Field Interpretation of High-Spin Trigonal-Bipyramidal Cobalt(II) Complexes

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Single-crystal polarized spectra have been recorded for a high-spin trigonal-bipyramidal  $\text{CoNS}_3\text{Br}$  chromophore. These spectra as well as those of the chromophores  $\text{CoNP}_3\text{Br}$  and  $\text{CoNN}_3\text{Br}$  have been interpreted on the basis of ligand field and angular overlap parameters. These parameters, which have been estimated either from metal-ligand orbital overlaps or from the experimental transitions, are quite meaningful for the interpretation of the coordination bond. In particular, it appears that the metal to ligand  $\pi$  bonding is significant for both sulfur and phosphorus donor atoms. A comparison between the point charge model where the radial integral ratio  $I_2/I_4$  is held constant within a given chromophore and the angular overlap model is presented.

### Introduction

High-spin trigonal-bipyramidal cobalt(II) complexes are particularly well suited for testing theoretical models, in that their electronic spectra show at least four well-separated absorption bands in the region 5–25  $\text{K}^{-1}$ .<sup>5</sup> Detailed assignments of these spectra can be obtained from single-crystal studies with polarized light when the crystal structure is known. Until now, single-crystal electronic spectra have been recorded for the  $[\text{Co}(\text{NCS})\text{Me}_6\text{tren}]\text{SCN}\cdot\text{H}_2\text{O}^2$  ( $\text{Me}_6\text{tren}$  = tris(2-dimethylaminoethyl)amine, chromophore  $\text{CoN}_5$ ) and  $[\text{CoBr}(\text{NP}_3)]\text{PF}_6^3$  ( $\text{NP}_3$  = tris(2-diphenylphosphinoethyl)amine, chromophore  $\text{CoNP}_3\text{Br}$ ) complexes. We report here single-crystal spectra of the  $[\text{CoBr}(\text{NS}_3)]\text{PF}_6$  ( $\text{NS}_3$  = tris(2-*tert*-butylthioethyl)amine, chromophore  $\text{CoNS}_3\text{Br}$ ) complex.<sup>6</sup>

The X-ray structure is known also for the trigonal-bipyramidal  $[\text{CoBr}(\text{Me}_6\text{tren})]\text{Br}$  complex<sup>7</sup> (chromophore  $\text{CoNN}_3\text{Br}$ ) which crystallizes in the cubic system and therefore cannot be investigated by means of single-crystal spectroscopy. However, the spectral assignment of this complex is supported by the assignment of the spectra of the thiocyanate analog. Therefore there are three chromophores,  $\text{CoNN}_3\text{Br}$ ,  $\text{CoNS}_3\text{Br}$  and  $\text{CoNP}_3\text{Br}$ , which have been shown to be similar in geometry,<sup>6-8</sup> to have the same axial donor atoms (N and Br), and to have spectral assignments supported by single-crystal studies. A comparison of the electronic transitions of these three complexes is quite instructive as well as the interpretation of the transition energies in terms of angular overlap parameters,<sup>9-11</sup> which can give significant information on the coordination bond.<sup>12</sup>

### Experimental Section

Single crystals of  $[\text{CoBr}(\text{NS}_3)]\text{PF}_6$  were grown by slow evaporation of acetone-ethanol solutions. Thin plates were obtained which crystallize<sup>6</sup> in the space group  $P2_1/n$ ;  $a = 27.420 \text{ \AA}$ ,  $b = 11.923 \text{ \AA}$ ,  $c = 17.082 \text{ \AA}$ ,  $\beta = 102.4^\circ$ , and  $Z = 8$ . In the unit cell there are two asymmetric units  $\text{CoBr}(\text{NS}_3)$  which are slightly misaligned. The two Co-Br axes, assumed as  $z$  axes for the molecular coordinate systems,

Table I. Squares of the Projections of the Co-Br Axes along the Crystal Axes

	$a$	$b$	$c^*$
$\text{Co}_1\text{-Br}_1$	0.43	0.00	0.57
$\text{Co}_2\text{-Br}_2$	0.48	0.02	0.49

form an angle of  $12^\circ$ . The squares of the projections of the  $z$  axes along the crystal axes are reported in Table I.

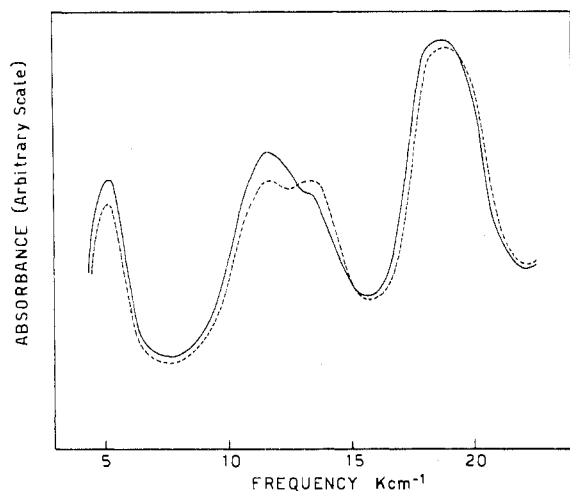
The polarized electronic spectra were recorded with the apparatus previously described<sup>3</sup> along the  $a$  and  $b$  crystal axes.

### Results and Discussion

**Electronic Spectra.** Figure 1 reports the electronic spectra of the  $\text{CoNS}_3\text{Br}$  chromophore recorded with the light polarized parallel to  $a$  and  $b$  crystal axes.

According to the figures of Table I the spectrum recorded with the electric vector of polarized light parallel to  $b$  has to be  $\perp$  polarized, while the spectrum parallel to  $a$  has to be almost equally  $\parallel$  and  $\perp$  polarized. Since the ground level of a Co(II) complex in  $C_{3v}$  symmetry is expected to be  $^4A_2$ , the bands at 5.2, 11.8, and 18.8 kK can be assigned to the  $^4A_2 \rightarrow ^4E$  transitions. The lack of neat polarization properties for the  $^4A_2 \rightarrow ^4E$  transitions is not uncommon, as transitions to degenerate levels are very sensitive to low-symmetry components.<sup>2,3,13,14</sup> The main difference in the spectrum recorded parallel to  $a$ , as compared to that parallel to  $b$ , is the appearance of the 13.8-kK band. With the figures of Table I in mind this is reasonably assigned to a polarized  $^4A_2 \rightarrow ^4A_2$  transition.

The present assignment corresponds quite closely to those previously proposed for the analogous  $\text{CoNN}_3\text{Br}$  and  $\text{CoNP}_3\text{Br}$  chromophores,<sup>2,3</sup> as shown in Figure 2 and Table II. Although these three chromophores can be described as trigonal bipyramidal, they show significant departures from  $D_{3h}$  symmetry. In fact the  $\text{N}_{ax}\text{-Co-L}_{eq}$  angle ( $\alpha$ ) is in every case less than  $90^\circ$ . The most highly distorted in this sense is the  $\text{CoNP}_3\text{Br}$  chromophore, where the angle  $\alpha$  is  $74^\circ$  and the Co-N distance is so large (Table III) that the chromophore



**Figure 1.** Single-crystal polarized electronic spectra of the  $\text{CoNS}_3\text{-Br}$  chromophore: —, spectrum recorded along  $b$ ; ---, spectrum recorded along  $a$ .

**Table II.** Observed and Calculated Energies of the Transitions of the Trigonal-Bipyramidal High-Spin Cobalt(II) Complexes and Ligand Field Parameters<sup>a</sup>

	Transition Energies					
	$\text{CoNN}_3\text{Br}$		$\text{CoNS}_3\text{Br}$		$\text{CoNP}_3\text{Br}$	
	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd
$A_2 \rightarrow A_1$		3.2		3.0		4.8
$A_2$		4.8		4.9	9	9.3
E	5.7	5.3	5.2	4.9	5.7	6.0
E	12.3	12.3	11.8	11.8	10.0	9.7
$A_2$	16.1	15.7	13.8	14.0	13.3	13.3
E	19.5	19.5	18.8	18.7	17.5	17.4
Donor Parameters						
	$\text{CoNN}_3\text{Br}$		$\text{CoNS}_3\text{Br}$		$\text{CoNP}_3\text{Br}$	
$N_{axial} \{e'_\sigma, e'_\pi\}$	3.8, 0		3.1, 0		0.9, 0	
$\{Dq, I_2\}$	1.14, 3.8		0.93, 3.1		0.27, 0.9	
$Br \{e'_\sigma, e'_\pi\}$	5.1, 2.04		5.0, 2.0		5.4, 2.34	
$\{Dq, I_2\}$	0.71, 7.14		0.7, 7.0		0.68, 7.74	
$L^b \{e'_\sigma, e'_\pi\}$	4.2, 0		3.54, -0.63		3.68, -0.83	
$\{Dq, I_2\}$	1.26, 4.2		1.31, 2.91		1.44, 2.85	
$\beta$	0.75		0.68		0.55	

<sup>a</sup> The range of variability of these parameters is reported in the text. All the calculations were performed using a  $C_{3v}$  symmetry field, with N-Co-L angles as found in the X-ray structure determination (see Table III). All values are in kK except  $\beta$  which is dimensionless. <sup>b</sup> L represents the equatorial donor.

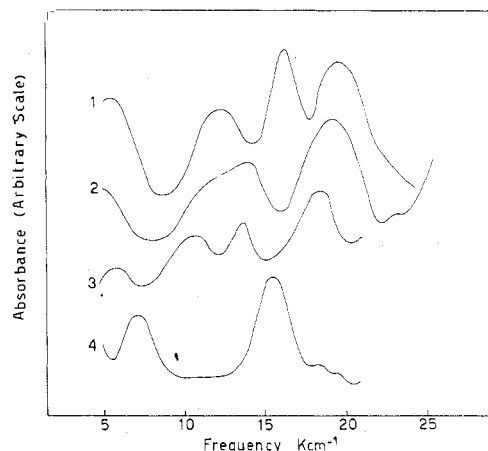
**Table III.** Structural Parameters for  $\text{CoNL}_3\text{Br}$  Chromophores

	L = S	L = P	L = N
Co-N, Å	2.26	2.76	2.15 <sup>a</sup>
Co-Br, Å	2.39	2.36	2.43
N-Co-L, deg	81.5 ( $\pm 1$ ) <sup>b</sup>	74 ( $\pm 1$ ) <sup>b</sup>	81.1 (0.8) <sup>c</sup>

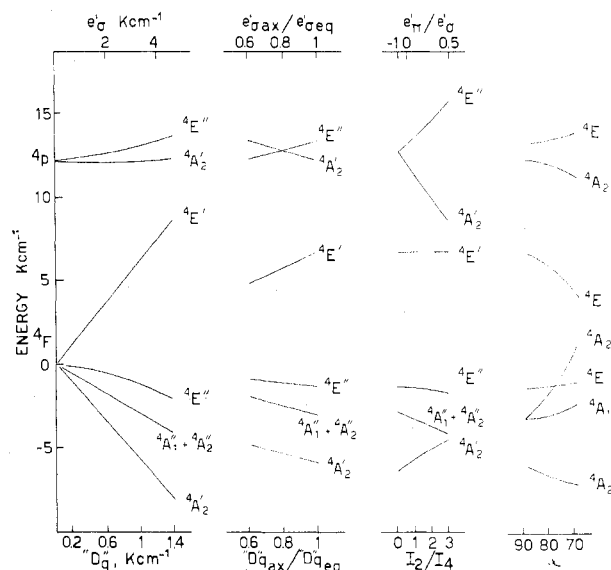
<sup>a</sup> The Co-N(equatorial) distance is 2.08 Å. <sup>b</sup> Average value. <sup>c</sup> Standard deviation.

$\text{CoNP}_3\text{Br}$  is quasitetrahedral.<sup>8,15</sup> In the  $\text{CoNN}_3\text{Br}$  and  $\text{CoNS}_3\text{Br}$  chromophores the  $\alpha$  angles are  $\sim 81^\circ$ , though they differ in the Co-N and Co-Br distances, as shown in Table III. In general, as the electronegativity of the equatorial ligand diminishes, the Co-N distance increases and the Co-Br distance decreases. Owing to the distortion toward a tetrahedron of these complexes the spectra of the tribromoquinoline cobaltate complex (chromophore  $\text{CoNBr}_3$ , tetrahedral trigonally distorted) have been also included for comparison purposes. The d-d transitions of the latter complex had been previously assigned on the basis of single-crystal data.<sup>13</sup>

The values of the transitions reported in Table II show how the energy of the first  $A_2 \rightarrow E$  transition is little affected by



**Figure 2.** Diffuse reflectance spectra of the  $\text{CoNN}_3\text{Br}$  (1),  $\text{CoNS}_3\text{Br}$  (2),  $\text{CoNP}_3\text{Br}$  (3), and  $\text{CoNBr}_3$  (4) chromophores.



**Figure 3.** Energy level diagrams for a cobalt(II) complex in  $D_{3h}$  symmetry as functions of crystal field and angular overlap parameters (see eq 2 and 3 of text):  $Dq(ax)/Dq(eq) = 1$ ,  $I_2/I_4 = 0.55$ ,  $\beta = 0.85$ . From the left to the right are the effect of changing the  $Dq(ax)/Dq(eq)$  ratio, the  $I_2/I_4$  ratio and the  $N_{ax}\text{-Co-L}(\alpha)$  angle.

structural variations throughout the series, whereas the second  $A_2 \rightarrow E$  transition, as well as the two  $F \rightarrow P$  transitions, shifts to lower frequency as the tetrahedral distortion increases. The separation between the  $F \rightarrow P$  transitions follows, however, a less regular pattern: it is 3.4 kK for the  $\text{CoNN}_3\text{Br}$  chromophore, 5.0 kK for  $\text{CoNS}_3\text{Br}$ , and 4.2 kK for  $\text{CoNP}_3\text{Br}$ , whereas no splitting is observed for the  $\text{CoNBr}_3$  chromophore. Furthermore in the spectrum of the  $\text{CoNP}_3\text{Br}$  chromophore there is evidence of a  ${}^4A_2 \rightarrow {}^4A_2$  band at  $\sim 9$  kK.

**Fitting of the Transitions.** In order to account for the trends observed in the spectra of this series of complexes, ligand field calculations were performed in the additivity scheme.<sup>11</sup> The crystal field and angular overlap parametrizations have been shown to be equivalent, in the sense that under some conditions a one to one correspondence can be made between the two sets of parameters.<sup>11</sup> Since either model can be more convenient in expressing the ligand field energies, depending on the symmetry of the complex and the nature of the donor atoms, we have reported the energy level diagrams as functions of both crystal field and angular overlap parameters.<sup>16</sup> The  $e'_\sigma$  and  $e'_\pi$  parameters have been defined by Schaffer.<sup>17</sup> The crystal field parameters<sup>11</sup> are  $I_2$  and " $Dq$ " =  $I_4/6$ . In these diagrams (Figure 3) the  $I_2/I_4$  ratio (or  $e'_\sigma/e'_\pi$ ) are kept constant for the

five donor atoms. Even with this approximation these diagrams show, for example, that the second  $^4A_2$  level becomes more separated from the ground-state level, and the range of the d-d transitions decreases, by increasing the tetrahedral distortion, as has been observed. The separation of the F  $\rightarrow$  P transitions, as referred to these diagrams, will be discussed later. For a quantitative fitting of the observed transitions, both the crystal field and the angular overlap models require six parameters, two for each independent donor atom, plus the nephelauxetic  $\beta$ . The angular overlap parameters are  $e'_{\sigma N}$ ,  $e'_{\pi N}$ ,  $e'_{\sigma Br}$ ,  $e'_{\pi Br}$ ,  $e'_{\sigma L}$ , and  $e'_{\pi L}$  (L is the equatorial donor), and we will refer to them in the following discussion. The number of parameters is clearly too high in comparison with the number of independent electronic transitions in  $C_{3v}$  symmetry, which is two.<sup>18</sup> It is possible however to make some assumptions which reduce the number of freely adjustable parameters. The validity of these assumptions may be checked by transferring the values among the complexes of the series. The first assumption is to set  $e'_{\pi N} = 0$  since the nitrogen donor atoms are tertiary nitrogens.<sup>19</sup> A further simplification can be introduced by assuming, as has already been done,<sup>12,20</sup> that the bromine orbitals involved in the coordinative bond are essentially p orbitals. In this case the  $e'_{\pi Br}$  can be expressed in terms of the  $e'_{\sigma Br}$  parameter through the relation

$$e'_{\pi Br} = (S_{\pi}/S_{\sigma})^2 e'_{\sigma Br} \quad (1)$$

where  $S_{\lambda}$  is the donor-ligand overlap.

Finally it is assumed that the charge distribution does not change that much among several complexes so that for each donor atom  $e'_{\sigma} = KS_{\sigma}^2$ ,<sup>21</sup> where  $K$  is a constant. Once  $K$  is known, it is possible to calculate  $e'_{\sigma}$  as function of the metal-donor distance. In the case of the bromine, the  $K$  value can be evaluated using the data available for the pseudooctahedral  $CoBr_2$  complex. The  $S_{\sigma}$  and  $S_{\pi}$  values are calculated using the Co-Br distance of 2.60 Å<sup>22</sup> and  $e'_{Br}$  and  $e'_{\pi Br}$  are calculated through eq 1 and 2,  $Dq$  being 640 cm<sup>-1</sup>.<sup>23</sup> The

$$^{10}/_6 I_4 = 10Dq = 3e'_{\sigma} - 4e'_{\pi} \quad (2)$$

overlaps  $S_{\sigma}$  and  $S_{\pi}$  between the cobalt d orbitals and the bromine p orbitals were computed using the Clementi's double- $\zeta$  functions. The charges have been taken equal to zero, as the overlap is only slightly affected by the charge distribution.<sup>20</sup> In this way we are left with only three parameters in the general case:  $e'_{\sigma N}$ ,  $e'_{\pi L}$ , and  $e'_{\sigma L}$ .

Considering now the  $CoNN_3Br$  chromophore, the equatorial ligand is also a tertiary nitrogen atom, allowing us to set  $e'_{\pi L} = 0$ . At this point the number of freely adjustable parameters has been reduced to two, and a meaningful fitting of the transitions can be attempted. Optionally, the  $e'_{\sigma N(axial)}/e'_{\sigma N(equatorial)}$  can be calculated from the square of the cobalt (d)-nitrogen (p) overlaps, leaving us with only one parameter  $e'_{\sigma N}$ . In both cases insignificantly different fittings of the transitions were obtained. The calculations were performed using  $C_{3v}$  symmetry and the  $\alpha$  angle as found in the X-ray structure determination (Table III). A reasonable fitting has been obtained (Table II) for  $\beta = 0.75$  and  $e'_{\sigma N(equatorial)} = 4200$  cm<sup>-1</sup>. Such  $e'_{\sigma}$  values correspond to a  $Dq$  value of 1260 cm<sup>-1</sup>. If it is kept in mind that the Co-N distance is sensibly shorter here than in octahedral complexes, this  $Dq$  value is quite acceptable. For example the  $Ni(en)_3^{2+}$  complex has Ni-N(amine) distances of 2.13 Å<sup>24</sup> and  $Dq$  of 1130 cm<sup>-1</sup>.<sup>25</sup> This value is coincident with  $Dq(axial)$  (1130 cm<sup>-1</sup>) in the present  $CoNN_3Br$  complex, where the Co-N(axial) distance is 2.15 Å.

The success of this method, despite the drastic approximations introduced, encouraged us to transfer the  $e'_{\sigma N}$  for the chromophores  $CoNS_3Br$  and  $CoNP_3Br$  so that only the parameters  $e'_{\sigma L}$ ,  $e'_{\pi L}$ , and nephelauxetic  $\beta$  are left to be de-

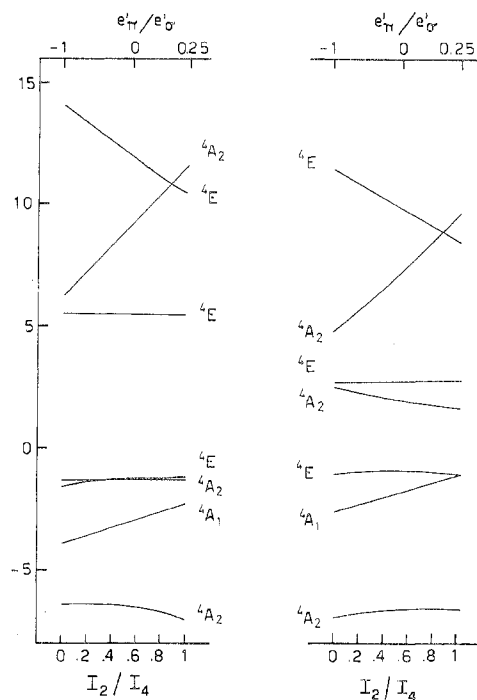


Figure 4. Energy level diagrams showing the effect of changing the  $e'_{\pi}/e'_{\sigma}$  ratio of the equatorial donors for constant  $Dq$ : left, the  $CoNS_3Br$  chromophore ( $e'_{\sigma N} = 3.1$  kK,  $e'_{\sigma Br} = 5.0$  kK,  $e'_{\pi Br} = 2.0$  kK,  $Dq_S = 1.33$  kK,  $\beta = 0.70$ ,  $\alpha = 82^\circ$ ); right, the  $CoNP_3Br$  chromophore ( $e'_{\sigma N} = 0.9$  kK,  $e'_{\sigma Br} = 5.4$  kK,  $e'_{\pi Br} = 2.34$  kK,  $Dq_P = 1.37$  kK,  $\beta = 0.55$ ,  $\alpha = 75^\circ$ ).

termined from the observed transitions. In this approach the equatorial donors are treated as if they were linearly ligating.

For the chromophore  $CoNS_3Br$ , using the values  $e'_{\sigma N} = 3100$  cm<sup>-1</sup>,  $e'_{\sigma Br} = 5000$  cm<sup>-1</sup>, and  $e'_{\sigma Br}/e'_{\pi Br} = 2.5$ , satisfactory fittings of transitions were found for  $\beta = 0.65-0.70$ ,  $e'_{\sigma S} = 3400-3600$  cm<sup>-1</sup>, and  $e'_{\sigma S}/e'_{\pi S} = -(5-7)$ . No fit was found for positive values of  $e'_{\pi S}$  as the energy levels strongly depend on the  $e'_{\sigma}/e'_{\pi}$  ratio used for the sulfur atom (see Figure 4). If  $e'_{\pi}$  is interpreted as the antibonding effect on the metal orbitals, the negative sign is indicative of bonding interaction with high-energy empty orbitals of sulfur. This would suggest that the d orbitals of sulfur are involved in the bonding. A significant fit is reported in Table II.

For the chromophore  $CoNP_3Br$ , using the values  $e'_{\sigma N} = 900$  cm<sup>-1</sup>,  $e'_{\sigma Br} = 5400$  cm<sup>-1</sup>, and  $e'_{\sigma Br}/e'_{\pi Br} = 2.3$ , satisfactory fittings of the transitions were found for  $\beta = 0.55-0.60$ ,  $e'_{\sigma P} = 3200-3700$  cm<sup>-1</sup>, and  $e'_{\sigma P}/e'_{\pi P} = -(3-6)$ , the lower  $e'_{\sigma P}/e'_{\pi P}$  ratios corresponding to the lower  $e'_{\sigma P}$  values. Also in the present case no fit was found for positive  $e'_{\pi P}$  suggesting an involvement of the d orbitals of phosphorus in the bond as already proposed.<sup>26,27</sup>

In both the  $CoNS_3Br$  and  $CoNP_3Br$  chromophores the calculated energy of the  $^4A_2 \rightarrow ^4A_2(F)$  transition is somewhat uncertain given its drastic dependence on the N-Co-L angle; since these chromophores do not have strict  $C_{3v}$  symmetry we have used an average value of the three observed N-Co-L angles.

It may be concluded, therefore, that angular overlap calculations have provided satisfactory fittings in the series of complexes studied, giving sets of parameters which are quite reasonable from the chemical point of view<sup>10,28</sup> and can be transferred from one chromophore to another with some confidence if the donors approximate linearly ligating donors and the interligand overlap is small.<sup>12,29</sup> Using eq 2 and 3 the

$$I_2 = e'_{\sigma} + e'_{\pi} \quad (3)$$

AO parameters can be transferred into the crystal field

language. Also these values are reported in Table II. We use the "Dq" although it has a different meaning from Dq of the point charge model, since it is familiar to the inorganic chemist.<sup>30</sup> The "Dq" values for tertiary nitrogen and thioetheral sulfur are quite close to each other in substantial accord with previous findings.<sup>31</sup> The position of phosphorus in the spectrochemical series is not well settled. The present results suggest it should be on the high-field side of the amine nitrogen. The series for I<sub>2</sub> appears to be Br > N > S ≥ P.

Finally it is interesting to compare the values of I<sub>2</sub>, I<sub>4</sub>, and "Dq" with those straightforwardly obtainable from the general ligand field diagrams of Figure 3, where, owing to the large number of parameters, I<sub>2</sub>/I<sub>4</sub> is assumed equal for all the donors within a chromophore.<sup>32</sup> This restrictive condition requires an increase of the I<sub>2</sub>/I<sub>4</sub> ratio in going from CoNN<sub>3</sub>Br to CoNP<sub>3</sub>Br in order to account for the large separation between the F → P transitions (see Figure 2). These results are in contrast with those obtained when the appropriate I<sub>2</sub>/I<sub>4</sub> ratio is considered for each donor atom. The comparison between the two types of calculations represents a meaningful example of the type of errors made when simple crystal field calculations (I<sub>2</sub>/I<sub>4</sub> constant within a chromophore) are used to fit the spectra in low-symmetry chromophores.

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**Registry No.** CoNS<sub>3</sub>Br, 53608-74-5; CoNN<sub>3</sub>Br, 34376-74-4; CoNP<sub>3</sub>Br, 52225-43-1.

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## Geometrical, Optical, and Conformational Isomers of Octahedral Metal Complexes Formed with a Linear Quadridentate Amine Ligand. The 3,2,3-tet System

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An extensive series of metal complexes of Co(III) (and one each of Rh(III) and Cr(III)) containing the linear quadridentate ligand 3,2,3-tet (NH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>NH(CH<sub>2</sub>)<sub>2</sub>NH(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub>) have been isolated, characterized, and obtained in optical forms. Four of the five possible stable isomers have been isolated, three of which were separated into optical isomers. These four isomers represent the basic cis-β and trans geometries which additionally display a secondary isomerism due to the meso and racemic configurations of the inner nitrogen atoms. Most of the complexes were of the type *trans-R,R',S,S'*-[Co(3,2,3-tet)XY]<sup>n+</sup>, where X and Y represent a wide variety of unidentate ligands. A number of these trans complexes have been resolved directly and most of the others have been obtained in optically active forms by chemical conversion. The absolute configurations of all the complexes have been unambiguously correlated by chemical interconversions. Various physical measurements are recorded which support the assigned stereochemistries. Equilibria data were obtained for the various geometrical and conformational isomers. It was found that the ligand preferred the racemic configuration of the inner racemic atoms in all stereochemistries, the most stable of which was the trans disposition of the ligand. These systems are relatively optically stable even when proton exchange occurs provided that the X and/or Y groups are not the aquo ligands. The presence of an aquo group leads to proton exchange and racemization even in concentrated acid solutions. The broad aspects of the racemization of the diaquo, hydroxoquo, and dihydroxo species have been studied kinetically. It was found that the hydroxoquo species in neutral water racemized faster than the dihydroxo species at pH 11.3 and that in 5 M perchloric acid the diaquo species racemized slowly but efficiently in the sense that proton exchange was only 5 times as fast as racemization.

Octahedral metal complexes formed with simple linear quadridentate amines potentially provide a diversity of possible geometrical and conformational isomers, many of which exist in resolvable species. The factors which determine the stability of these forms are subtle and complicated, and though a

number of recent attempts<sup>1-3</sup> have been made to interpret the stereochemical behavior of these systems, the interplay and the predominance of the various effects involved are poorly understood. In their thorough study of the cobalt complexes of the ligand 1,8-diamino-3,6-diazaoctane (trien), Sargeson