

benzene rings, and the ultraviolet spectrum should be that of unperturbed TRI. Bands are observed at 325 and 275 $m\mu$, and the spectrum is similar to that illustrated for isomer A. This suggests little if any interaction between benzene rings in isomer A and is consistent with its formulation as *meso*-Co(TRI)₃³⁺. It is probable that the different absorption pattern observed in the spectrum of isomer B, *dl*-Co(TRI)₃³⁺, results from

the interactions of overlapping benzene rings, as predicted.

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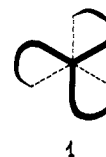
Evidence for Piper's Model of Optical Activity. The Structure and Absolute Configuration of (+)₅₄₆₁-Bis(tribenzo[*b,f,j*]-[1,5,9]triazacyclododecine)cobalt(III) Iodide¹

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Abstract: The absolute configuration of (+)₅₄₆₁-bis(tribenzo[*b,f,j*]-[1,5,9]triazacyclododecine)cobalt(III) iodide has been determined from an X-ray diffraction study. The symmetry of the complex ion is D₃, and like most other known trigonal (pseudo-octahedral) transition-metal complexes it possesses a small (8°) twist distortion about the threefold axis. This distortion is in the counterclockwise direction as is the case for Λ -(+)-Co(en)₃, which has a remarkably similar circular dichroism spectrum in the region of the ¹T_{1g} ← ¹A_{1g} and ¹T_{1g} ← ¹A_{1g} optical transitions of d⁶ octahedral cobalt(III). We suggest that this correspondence constitutes experimental support for Piper's model of optical rotation in trigonal complexes. The crystals studied belong to space group P2₁2₁2₁ with a₀ = 19.592 (3), b₀ = 14.609 (3), and c₀ = 14.508 (3) Å. The observed density was 1.79 g/cm³, with 1.74 g/cm³ calculated for four formula units in the cell. The structure was solved using 3297 statistically significant unique reflections collected by a counter method, and refined to a final R factor of 0.043. The mean Co-N bond is 1.923 (5) Å, and the mean distance between adjacent phenyl rings is 3.2 Å.

Trigonal cobalt(III) has been an important testing ground for theories,³⁻⁷ and models^{8,9} of optical rotation, with the goal being the determination of absolute configurations¹⁰⁻¹³ from the optical data. The pivotal point in the use of the optical data has been the assignment of the low-energy doublet generally observed at ca. 4800 Å in the circular dichroism (CD) spectra. Progress has been somewhat hampered, however, due to the need to rest heavily on studies of ions of the type Co(AA)₃ⁿ⁺, **1**, for which Saito, *et al.*,¹⁴ have provided



(1) (+)₅₄₆₁-Co(TRI)₃·3H₂O, where TRI is tribenzo[*b,f,j*]-[1,5,9]triazacyclododecine.

(2) (a) Riverside; (b) Portland.

(3) (a) T. S. Piper and A. G. Karipides, *Mol. Phys.*, **5**, 475 (1962); (b) A. G. Karipides and T. S. Piper, *J. Chem. Phys.*, **40**, 674 (1964); (c) T. S. Piper and A. G. Karipides, *Inorg. Chem.*, **4**, 923 (1965).

(4) (a) A. D. Liehr, *J. Phys. Chem.*, **68**, 665 (1964); (b) in "Transition Metal Chemistry," R. Carlin, Ed., Marcel Dekker, Inc., New York, N. Y., 1966, pp 166-338.

(5) C. Schäffer, *Proc. Roy. Soc., Ser. A*, **297**, 96 (1967).

(6) M. Shinada, *J. Phys. Soc. Jap.*, **19**, 1607 (1967).

(7) S. F. Mason and B. J. Norman, *Chem. Commun.*, **48** (1965).

(8) J. I. Legg and B. E. Douglas, *J. Amer. Chem. Soc.*, **88**, 2692 (1966).

(9) C. J. Hawkins and E. Larsen, *Acta Chem. Scand.*, **19**, 185 (1965).

(10) F. Woldbye in "Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry," G. Sznatzke, Ed., Heyden and Son, Ltd., London, 1967, pp 101-115.

(11) A. M. Sargeson in "Chelating Agents and Metal Chelates," F. P. Dwyer and D. P. Mellor, Ed., Academic Press, New York, N. Y., 1964, pp 183-235.

(12) S. F. Mason, *Quart. Rev. (London)*, **17**, 20 (1963).

(13) R. D. Gillard, *Chem. Brit.*, **3**, 205 (1967).

the basis of discussion through their determination of the absolute configuration of the (+)-Co(en)₃³⁺ ion. The major difficulty with the above system is the stereochemical flexibility of the chelate rings.¹⁵ Although the single crystal CD study of (+)-Co(en)₃³⁺ by Ballard, McCaffery, and Mason¹⁶ has resolved some of the uncertainties in the assignment of the doublet, *vide supra*, the ambiguities persist for solution spectra. Workers have, therefore, sought other criteria for judging assignments, the most widely used being the ion-pair effect.¹⁷⁻¹⁹ In brief, it has been proposed¹⁹ that the primary effect on the CD spectrum of adding an ion such as PO₄³⁻ to a solution of **1** is an increase in the intensity of the ¹A₂ ← ¹A₁ component of the trigonally split ¹T_{1g} ← ¹A_{1g} transition while the ¹E_a ← ¹A₁ com-

(14) K. Nakatsu, M. Shiro, Y. Saito, and H. Kuroya, *Bull. Chem. Soc. Jap.*, **30**, 158 (1957).

(15) A. J. McCaffery, S. F. Mason, and B. J. Norman, *Chem. Commun.*, **49** (1965).

(16) R. E. Ballard, A. J. McCaffery, and S. F. Mason, *Proc. Chem. Soc.*, **331** (1962).

(17) U. L. Smith and B. E. Douglas, *Inorg. Chem.*, **5**, 784 (1966).

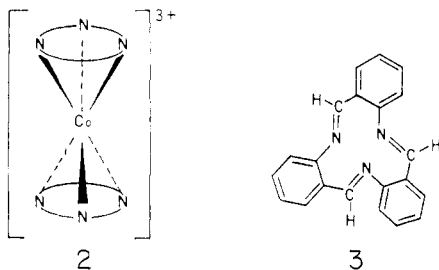
(18) K. Ogino, *Bull. Chem. Soc. Jap.*, **42**, 447 (1969).

(19) S. F. Mason and B. J. Norman, *Chem. Commun.*, **73** (1965).

ponent is virtually unchanged in intensity. Recent structural work on various $\text{Cr}(\text{en})_3^{3+}$ conformers implies that this effect is due to specific hydrogen bonding.²⁰

A dramatic illustration of the problems which can arise occurs in the tris(trimethylenediamine)cobaltate(III) complex. Saito, *et al.*,²¹ have determined the absolute configuration of the $(-)_5461$ optical isomer to be Λ with respect to chelate ring chirality. The crystal field, however, is slightly twisted in the opposite sense. Piper's model³ would thus predict a CD curve similar to that of $\Delta\text{Co}(\text{en})_3^{3+}$. Gollong and Hawkins'²² assignment of the very weak CD spectrum (based on the ion-pairing effect¹⁹) results in the opposite prediction. Since the salt effect is in all probability tied up with conformational changes of the metal complex,^{10,20} and there is no independent evidence as to the sign of the trigonal splitting, we cannot regard these results as the last word on the matter.

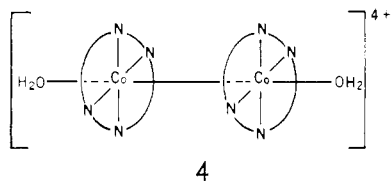
In contrast to the above we report the absolute configuration of a new trigonal complex of cobalt(III) which has an extremely different geometric array of chelate rings.²³ This compound $(+)_5461\text{-Co}(\text{TRI})_2$, **2**, where TRI, **3**, is the trimer formed by the self-conden-



sation of *o*-aminobenzaldehyde in the presence of metal ions, is stereochemically rigid. Although **1** and **2** are seemingly structurally unrelated, their $(+)_5461$ optical isomers have remarkably similar circular dichroism spectra. Thus, we have been prompted to search for a model that correctly relates the absolute configurations of $(+)_5461\text{-Co}(\text{TRI})_2^{3+}$ and $(+)_5461\text{-Co}(\text{en})_3^{3+}$.

Experimental Section

The compound thought to be $(+)_5461\text{-[Co(TAAB)}_2\text{]}_2 \cdot 2\text{H}_2\text{O}$, **4** (TAAB is the cyclic tetramer formed by *o*-aminobenzaldehyde), a reddish-brown powder supplied by S. C. Cummings, was



dissolved in an acidified aqueous solution and filtered. The filtrate was evaporated slowly and a small quantity of burgundy-colored crystals were obtained. One of these, having dimensions approximately $0.2 \times 0.2 \times 0.4$ mm, was mounted and proved satisfactory for collection of all data. Precession photographs revealed orthorhombic symmetry, and the systematic absences $h00$, $h \neq 2n$, $0k0$,

(20) K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, **7**, 842 (1968).

(21) T. Nomura, F. Marumo, and Y. Saito, *Bull. Chem. Soc. Jap.*, **42**, 1016 (1969).

(22) J. R. Gollong and C. J. Hawkins, *Chem. Commun.*, 689 (1968).

(23) See the previous paper by S. C. Cummings and D. H. Busch for a discussion of the chemistry of this new compound.

$k \neq 2n$, and $00l$, $l \neq 2n$, uniquely determined the noncentrosymmetric space group $\text{P2}_12_12_1$ (D_2^4 , no. 19). The long axis was identified as the *c* axis, and faces parallel to it included $\{100\}$, $\{110\}$, and $\{1\bar{1}0\}$.

The crystal was moved to a computer-controlled²⁴ automated Picker diffractometer where 12 reflections, having θ ($\text{Mo K}\beta_1$) $> 10^\circ$, were centered in the detector window. The observed angular settings indicated the unit cell parameters were $a = 19.592 \pm 0.007$, $b = 14.609 \pm 0.003$, $c = 14.508 \pm 0.003$, $V = 4152.5 \text{ \AA}^3$ ($\text{Mo K}\beta_1 = 0.63225 \text{ \AA}$). The observed density of 1.79 g/cm^3 , determined by flotation, corresponds to a *Z* of 3.23 for the presumed formula $(+)_5461\text{-[Co(TAAB)}_2\text{]}_2 \cdot 2\text{H}_2\text{O}$; using the formula $\text{Co}(\text{TRI})_2 \cdot 3\text{H}_2\text{O}$ and a *Z* of 4, the calculated density is 1.74 g/cm^3 .

Six octants of data were collected using niobium-filtered $\text{Mo K}\alpha$ radiation, with θ ($\text{Mo K}\alpha$) $\leq 22.5^\circ$, a takeoff angle of 4° , and the pulse height discriminator set to accept 95% of the $\text{Mo K}\alpha$ radiation, when centered on the $\text{K}\alpha$ peak. The moving crystal, moving counter technique was used, with a 2θ scan rate of $1^\circ/\text{min}$ and scan range of $(1.33 + \Delta)$, where Δ is included to account for the 2θ separation of the $\text{K}\alpha_1$ and $\text{K}\alpha_2$ peaks at the value of $\sin \theta/\lambda$ for the reflection concerned; this conformed well with the mosaic spread of the crystal. The crystal-source and crystal-detector distances were each approximately 24 cm; 1.5-mm diameter incident and exit beam collimators were used without further restriction on the aperture. Background counts of 10 sec each were measured at the extremes of each 2θ scan. The observed intensities²⁵ were $I = A(P - (t/20)B)$, where *A* is the correction factor for attenuators inserted for those reflections having counting rates which would otherwise exceed the linear counting range of the detector, *P* is the number of counts during the scan, *B* is the sum of the background counts, and *t* is the counting time for the scan in seconds. Three standard reflections, measured every 50 reflections, showed only statistical fluctuations during the collection of the intensity data. In all, 18,468 reflections were measured, of which 6155 unique reflections remained after averaging equivalent data. Of these, 3297 (including 1500 Bijvoet pairs) were accepted under the criterion $I \geq 2.5(P + (t^2/400)B)^{1/2}$ for all equivalent reflections. The observed intensities were corrected for Lorentz and polarization effects and an absorption correction gave calculated transmission factors ranging from 0.63 to 0.70.

Spectra obtained from a solution of one single crystal $0.2 \times 0.2 \times 0.5$ mm taken from the same crop of crystals described above were identical with those reported for $(+)_5461\text{-Co}(\text{TRI})_2$ ²³ before recrystallization, *vide supra*, and with those observed on a bulk solution of the recrystallized sample. The spot intensities in the $hk0$, $h0l$, and $0kl$ zones collected on films before the crystal was dissolved were in agreement with the counter intensity data. The ORD and CD spectra were taken in aqueous solution in a 1-cm quartz cell using a Jasco Model ORD/UV/CD-5 spectrophotometer. The specific rotations observed in the bulk recrystallized sample were ca. 40% larger than for the original material indicating an additional 20% resolution during crystallization.

Solution and Refinement of the Structure

A three-dimensional map of the Patterson function²⁶ was solved for four heavy atoms, which were assumed to be iodine atoms. A Fourier map phased on these atoms indicated that three had an electron density nearly quadruple that of the fourth, leading to a reassignment of the fourth as a cobalt atom. Four coplanar atoms of the inner coordination sphere of cobalt were evident but attempts to find other atoms of a TAAB ligand were unsuccessful. At this point a comparison of calculated and observed structure factors^{27a,28} gave $R_1 =$

(24) The Busing and Levy programs for four-circle diffractometers were used for data collection: W. R. Busing and H. A. Levy, *Acta Cryst.*, **22**, 457 (1967).

(25) Data reduction and averaging of equivalent reflections were accomplished using the program REDAT, by L. Clifford, R. Eiss, and R. Short, 1968.

(26) Patterson and Fourier maps were calculated using the program FORDAP, by A. Zalkin.

(27) Structure factor calculations and least-squares refinement of parameters was carried out using (a) SFLS5, by C. T. Prewitt; and (b) ORFLS by W. R. Busing, K. O. Martin, and H. A. Levy, ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(28) The scattering factors and corrections for anomalous scattering by cobalt and iodine are from D. T. Cromer and J. T. Waber, *Acta*

Table I. Final Parameters in $\text{Co}(\text{C}_{21}\text{H}_{16}\text{N}_3)_2\text{I}_3 \cdot 3\text{H}_2\text{O}$

Atom	x^a	y	z	$B^{b,c}$
Co	0.06890 (10)	0.45368 (14)	0.47052 (13)	
N _{1A}	0.0000 (6)	0.4492 (8)	0.5621 (7)	1.7 (2)
N _{2A}	0.1003 (6)	0.5654 (8)	0.5302 (8)	1.9 (3)
N _{3A}	0.1256 (6)	0.3884 (8)	0.5567 (7)	1.5 (2)
C _{11A}	-0.0437 (8)	0.5287 (11)	0.5750 (11)	2.1 (3)
C _{12A}	-0.1157 (9)	0.5129 (12)	0.5886 (12)	3.9 (4)
C _{13A}	-0.1542 (9)	0.6023 (13)	0.6008 (12)	4.1 (4)
C _{14A}	-0.1229 (9)	0.6864 (12)	0.5986 (11)	3.5 (4)
C _{15A}	-0.0539 (9)	0.6912 (12)	0.5859 (11)	3.2 (4)
C _{16A}	-0.0157 (7)	0.6131 (11)	0.5736 (10)	1.9 (3)
C _{17A}	0.0601 (8)	0.6271 (12)	0.5664 (11)	3.1 (4)
C _{21A}	0.1709 (8)	0.5814 (12)	0.5382 (11)	2.8 (4)
C _{22A}	0.1991 (8)	0.6706 (11)	0.5284 (11)	2.5 (3)
C _{23A}	0.2663 (9)	0.6825 (13)	0.5450 (12)	4.1 (4)
C _{24A}	0.3076 (9)	0.6118 (14)	0.5745 (13)	4.2 (5)
C _{25A}	0.2831 (9)	0.5203 (13)	0.5862 (12)	3.7 (4)
C _{26A}	0.2104 (8)	0.5052 (11)	0.5667 (11)	2.2 (4)
C _{27A}	0.1851 (8)	0.4144 (11)	0.5861 (11)	2.4 (4)
C _{31A}	0.1017 (7)	0.3024 (11)	0.5931 (10)	2.2 (3)
C _{32A}	0.1425 (8)	0.2251 (11)	0.6033 (11)	2.6 (4)
C _{33A}	0.1159 (8)	0.1457 (11)	0.6421 (11)	3.3 (4)
C _{34A}	0.0470 (8)	0.1427 (12)	0.6689 (12)	3.6 (4)
C _{35A}	0.0069 (8)	0.2166 (11)	0.6640 (11)	3.2 (4)
C _{36A}	0.0309 (8)	0.3005 (12)	0.6216 (11)	3.3 (4)
C _{37A}	-0.0130 (7)	0.3833 (11)	0.6140 (10)	2.3 (3)
N _{1B}	0.1408 (6)	0.4471 (9)	0.3786 (8)	2.5 (3)
N _{2B}	0.0226 (6)	0.5258 (8)	0.3807 (8)	1.9 (3)
N _{3B}	0.0277 (6)	0.3495 (9)	0.4115 (8)	2.3 (3)
C _{11B}	0.1699 (8)	0.5310 (11)	0.3482 (11)	2.6 (4)
C _{12B}	0.2402 (7)	0.5411 (10)	0.3400 (11)	2.3 (3)
C _{13B}	0.2647 (7)	0.6254 (11)	0.3056 (10)	2.7 (4)
C _{14B}	0.2197 (8)	0.6948 (12)	0.2823 (11)	2.9 (4)
C _{15B}	0.1478 (8)	0.6810 (11)	0.2910 (10)	3.0 (4)
C _{16B}	0.1222 (8)	0.5986 (10)	0.3226 (11)	2.1 (3)
C _{17B}	0.0496 (7)	0.5856 (10)	0.3277 (11)	2.0 (3)
C _{21B}	-0.0522 (8)	0.5171 (12)	0.3711 (12)	3.3 (4)
C _{22B}	-0.0945 (8)	0.5920 (11)	0.3642 (11)	2.8 (4)
C _{23B}	-0.1648 (9)	0.5767 (12)	0.3571 (12)	3.8 (4)
C _{24B}	-0.1880 (9)	0.4866 (13)	0.3551 (13)	4.6 (5)
C _{25B}	-0.1469 (9)	0.4108 (12)	0.3605 (11)	3.5 (4)
C _{26B}	-0.0766 (8)	0.4257 (11)	0.3737 (11)	2.7 (4)
C _{27B}	-0.0340 (8)	0.3476 (12)	0.3772 (11)	3.1 (4)
C _{31B}	0.0672 (8)	0.2707 (11)	0.4006 (10)	2.6 (3)
C _{32B}	0.0441 (8)	0.1818 (13)	0.4169 (12)	3.8 (4)
C _{33B}	0.0855 (9)	0.1041 (13)	0.4037 (12)	4.4 (4)
C _{34B}	0.1549 (9)	0.1164 (12)	0.3733 (11)	4.1 (4)
C _{35B}	0.1815 (8)	0.2034 (12)	0.3552 (11)	3.1 (4)
C _{36B}	0.1400 (8)	0.2784 (11)	0.3708 (10)	2.8 (4)
C _{37B}	0.1663 (7)	0.3713 (11)	0.3496 (10)	2.4 (3)
I ₁	0.00156 (7)	0.34333 (9)	0.14539 (9)	
I ₂	0.36581 (7)	0.12768 (9)	0.17251 (9)	
I ₃	0.34031 (7)	0.29555 (11)	0.49184 (10)	
O ₁	0.1747 (6)	0.8871 (3)	0.4264 (8)	5.4 (3)
O ₂	0.3271 (6)	0.3485 (9)	0.2628 (8)	5.4 (3)
O ₃	0.4115 (7)	0.5088 (10)	0.2494 (9)	6.8 (4)

^a Estimated standard deviation of last significant figures in parentheses. ^b All temperature factors are in units of \AA^2 with $B_{ij} = 4B_{ij}/a_i^*a_j^*$ and $T_r = \exp[-(h^2b_{11} + k^2b_{22} + l^2b_{33} + 2hkb_{12} + 2hbl_{13} + 2lkb_{23})]$. ^c The heavy atom thermal parameters are given below.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	1.59 (9)	1.91 (11)	1.96 (10)	0.23 (9)	0.04 (8)	-0.10 (9)
I ₁	3.83 (6)	6.54 (8)	5.43 (7)	0.83 (7)	1.28 (6)	1.71 (7)
I ₂	5.41 (7)	3.48 (6)	5.75 (6)	-0.32 (6)	-2.20 (6)	0.42 (6)
I ₃	5.27 (7)	8.67 (10)	5.87 (8)	0.97 (8)	0.35 (7)	0.44 (9)

$\Sigma\{|F_o| - |F_c|\}/\Sigma|F_o| = 0.376$ where F_o is the observed and F_c the calculated structure factor. A cycle of least-squares refinement of atomic positional parameters, minimizing the function of $\Sigma w(|F_o| - |F_c|)^2$, was fol-

Cryst., 18, 104 (1965); D. T. Cromer, *ibid.*, 18, 17 (1965). For the other atoms the values are from "International Tables of X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England.

lowed by a second Fourier map which showed positions of 18 more atoms. At this point it was apparent that no TAAB ligand was present and that the cobalt atom was coordinated to two cyclic tridentate ligands. Another cycle of refinement of positional parameters and a difference Fourier map clearly indicated the remaining atoms of the two TRI ligands. Two further cycles of full-matrix refinement of positional and isotropic thermal parameters gave $R_1 = 0.093$, $R_2 = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2} = 0.105$, using a unit weighting scheme. A difference Fourier map showed four strong peaks remaining, three of which were subsequently refined as oxygens and represent waters of crystallization. The fourth gave unrealistically large temperature factors and was dropped. From this point on, the least-squares refinement was done at Riverside.^{27b}

Four more cycles of refinement using weighted data²⁹ reduced R_1 to 0.071 and R_2 to 0.075. At this point a test was made for the absolute configuration of the molecule by changing the indices of all reflections (hkl) to $(\bar{h}\bar{k}\bar{l})$. With this change one cycle of refinement led to convergence and gave $R_1 = 0.073$ and $R_2 = 0.078$. A Hamilton R test³⁰ on these values indicated the first choice to be significantly better at the 99.5% confidence level.

A difference electron density map computed at this stage gave clear indication of anisotropic motion of the cobalt and iodine atoms and gave images of most of the hydrogen atoms. A short-lived attempt (one cycle of refinement) was made in terms of refining the 30 unique TRI hydrogens but proved to be too expensive and of little interest. The heavy atoms were treated anisotropically, in the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$, and two cycles of refinement served to bring all parameters to convergence. The most prominent features on a final difference Fourier map were attributable to ligand hydrogen atoms. The final residuals were $R_1 = 0.043$ and $R_2 = 0.057$, and the standard deviation of an observation of unit weight was 1.76. The final observed and calculated structure factors have been deposited with NAPS.³¹

Atomic coordinates and thermal parameters have been listed in Table I. The ligand hydrogen atoms, although found, were not included in the refinement.

Results and Discussion

Structure of the Complex Cation. The $(+)_5461\text{-Co}(\text{TRI})_2^{3+}$ cation is shown in Figure 1. Selected bond distances and angles are given in Tables II and III, while the averaged geometry for the six equivalent *o*-aminobenzaldehyde fragments are shown in Figure 2.

The cobalt atom is coordinated to six nitrogens, three from each TRI ligand. The three nitrogens from each ligand define planes (Table IV) which are parallel to one another (2.36 \AA apart) with the cobalt sandwiched midway between. The three nitrogens of each TRI

(29) The weighting factors, w , for each reflection are given by $w = 4F^2/L^2\sigma(I)$, where L is the reciprocal Lorentz-polarization correction, and $\sigma(I) = [P + (I/20)^2B + (0.045I)^2]^{1/2}$.

(30) W. C. Hamilton, *Acta Cryst.*, 18, 502 (1965).

(31) A table of the observed and calculated structure amplitudes of $(+)_5461\text{-Co}(\text{TRI})_2 \cdot 3\text{H}_2\text{O}$ has been deposited as Document No. NAPS-00854 with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022. A copy may be secured by citing the document number, and by remitting \$3.00 for photoprints or \$1.00 for microfiche. Advance payment is required. Make checks or money orders payable to ASIS-NAPS.

Table II. Principal Intramolecular Bond Distances in $\text{Co}(\text{TRI})_2^{8+}$, Å

Bond	A. Bond Distances Involving One TRI Ligand					
	Ligand A			Ligand B		
	$m = 1, n = 3$	$m = 2, n = 1$	$m = 3, n = 2$	$m = 1, n = 3$	$m = 2, n = 1$	$m = 3, n = 2$
$\text{Co}-\text{N}_m$	1.89 (1)	1.95 (1)	1.93 (1)	1.94 (1)	1.91 (1)	1.92 (1)
N_m-C_{m1}	1.46 (2)	1.41 (2)	1.44 (2)	1.42 (2)	1.48 (2)	1.40 (2)
$\text{C}_{m1}-\text{C}_{m2}$	1.44 (2)	1.42 (2)	1.39 (2)	1.39 (2)	1.38 (2)	1.40 (2)
$\text{C}_{m2}-\text{C}_{m3}$	1.52 (3)	1.35 (2)	1.39 (2)	1.41 (2)	1.40 (2)	1.41 (3)
$\text{C}_{m3}-\text{C}_{m4}$	1.37 (2)	1.38 (3)	1.41 (2)	1.39 (2)	1.39 (2)	1.44 (2)
$\text{C}_{m4}-\text{C}_{m5}$	1.37 (2)	1.43 (3)	1.34 (2)	1.43 (2)	1.37 (3)	1.40 (2)
$\text{C}_{m5}-\text{C}_{m6}$	1.38 (2)	1.47 (2)	1.45 (2)	1.38 (2)	1.41 (2)	1.38 (2)
$\text{C}_{m6}-\text{C}_{m7}$	1.50 (2)	1.44 (2)	1.49 (2)	1.44 (2)	1.41 (2)	1.47 (2)
$\text{C}_{m1}-\text{C}_{m6}$	1.35 (2)	1.42 (2)	1.45 (2)	1.41 (2)	1.42 (2)	1.49 (2)
$\text{C}_{n7}-\text{N}_m$	1.25 (2)	1.31 (2)	1.30 (2)	1.29 (2)	1.28 (2)	1.31 (2)
N_m-N_n	2.62 (2)	2.64 (2)	2.66 (2)	2.68 (2)	2.59 (2)	2.62 (2)

B. Bond Distances between TRI Ligands			
Δ sense		Δ sense	
$\text{N}_{1A}-\text{N}_{3B}$	2.68 (2)	$\text{N}_{1A}-\text{N}_{2B}$	2.89 (2)
$\text{N}_{2A}-\text{N}_{2B}$	2.71 (2)	$\text{N}_{2A}-\text{N}_{1B}$	2.91 (2)
$\text{N}_{3A}-\text{N}_{1B}$	2.74 (2)	$\text{N}_{3A}-\text{N}_{3B}$	2.90 (2)

Table III

A. Bond Angles of Co Inner Coordination Sphere, Degrees					
Δ direction			Δ direction		
$\text{N}_{1A}-\text{Co}-\text{N}_{2A}$	86.7 (5)	$\text{N}_{1A}-\text{Co}-\text{N}_{3B}$	89.2 (5)	$\text{N}_{1A}-\text{Co}-\text{N}_{2B}$	99.2 (5)
$\text{N}_{2A}-\text{Co}-\text{N}_{3A}$	86.8 (5)	$\text{N}_{2A}-\text{Co}-\text{N}_{2B}$	89.5 (5)	$\text{N}_{2A}-\text{Co}-\text{N}_{1B}$	96.8 (5)
$\text{N}_{3A}-\text{Co}-\text{N}_{1A}$	86.5 (5)	$\text{N}_{3A}-\text{Co}-\text{N}_{1B}$	90.2 (5)	$\text{N}_{3A}-\text{Co}-\text{N}_{3B}$	98.0 (5)
$\text{N}_{1B}-\text{Co}-\text{N}_{2B}$	84.4 (5)	Average	89.6 (7)	Average	98.0 (12)
$\text{N}_{2B}-\text{Co}-\text{N}_{3B}$	86.2 (5)				
$\text{N}_{3B}-\text{Co}-\text{N}_{1B}$	87.7 (5)				
Average	86.3 (10)				

B. Bond Angles within TRI Ligand, Degrees						
Angle	Ligand A			Ligand B		
	$m = 1, n = 3$	$m = 2, n = 1$	$m = 3, n = 2$	$m = 1, n = 3$	$m = 2, n = 2$	$m = 3, n = 2$
$\text{Co}-\text{N}_m-\text{C}_{m1}$	119 (1)	119 (1)	119 (1)	117 (1)	119 (1)	118 (1)
$\text{Co}-\text{N}_m-\text{C}_{n7}$	126 (1)	124 (1)	126 (1)	123 (1)	126 (1)	125 (1)
$\text{N}_m-\text{C}_{m1}-\text{C}_{m2}$	118 (1)	122 (1)	124 (1)	121 (1)	122 (1)	125 (1)
$\text{N}_m-\text{C}_{m1}-\text{C}_{m6}$	119 (1)	115 (1)	116 (1)	115 (1)	114 (1)	120 (1)
$\text{C}_{m2}-\text{C}_{m1}-\text{C}_{m6}$	123 (1)	122 (1)	120 (1)	124 (1)	123 (1)	115 (1)
$\text{C}_{m1}-\text{C}_{m2}-\text{C}_{m3}$	111 (1)	119 (2)	120 (1)	117 (1)	118 (2)	123 (2)
$\text{C}_{m2}-\text{C}_{m3}-\text{C}_{m4}$	123 (2)	122 (2)	120 (1)	121 (1)	118 (2)	119 (2)
$\text{C}_{m3}-\text{C}_{m4}-\text{C}_{m5}$	119 (2)	123 (2)	122 (2)	120 (1)	125 (2)	121 (2)
$\text{C}_{m4}-\text{C}_{m5}-\text{C}_{m6}$	121 (2)	116 (2)	121 (2)	121 (1)	117 (2)	118 (1)
$\text{C}_{m5}-\text{C}_{m6}-\text{C}_{m7}$	116 (1)	116 (1)	122 (1)	119 (1)	117 (1)	119 (1)
$\text{C}_{m5}-\text{C}_{m6}-\text{C}_{m1}$	122 (1)	118 (1)	117 (1)	117 (1)	118 (1)	123 (1)
$\text{C}_{m1}-\text{C}_{m6}-\text{C}_{m7}$	122 (1)	126 (1)	121 (1)	123 (1)	124 (1)	117 (1)
$\text{C}_{n7}-\text{N}_m-\text{C}_{m1}$	115 (1)	116 (1)	115 (1)	119 (1)	114 (1)	117 (1)

ligand form an equilateral triangle; however, the triangles are rotated 8° from an octahedral configuration to give a twisted trigonal prism having the sense of a left-handed screw.

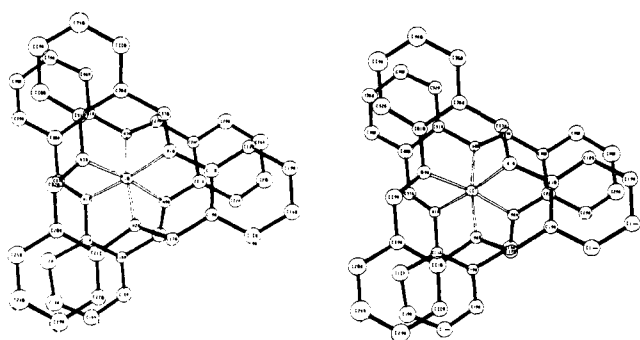


Figure 1. A stereopair showing the $(+)_{8461}\text{-Co}(\text{TRI})_2^{8+}$ ion as viewed along its threefold axis.

Each TRI ligand is propeller shaped with essentially the same conformation extant in $\text{Ni}(\text{TRI})(\text{H}_2\text{O})_3(\text{NO}_3)_2$.³² The mean pitch of the planar benzene is 14°

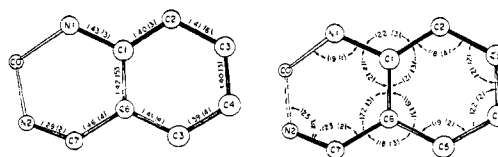


Figure 2. Mean distances and angles (average of six) in the repeating unit of the TRI ligand. The figures in brackets refer to the standard deviation of the six values used in calculating each average. The standard deviations of the mean are 0.01 Å for distances and $0.4\text{--}1.0^\circ$ for angles.

with respect to the nitrogen planes, with the sense being once again left-handed. The benzene pairs are opened

(32) E. B. Fleischer and E. Klem, *Inorg. Chem.*, **4**, 637 (1965).

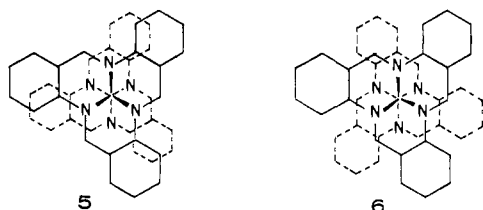
Table IV. Equations for Best Planes in TRI Ligands

Plane	Equation ^a
N _{1A} , N _{2A} , N _{3A}	0.0903X + 0.1633Y + 0.9824Z = 9.083
N _{1B} , N _{2B} , N _{3B}	0.0992X + 0.1738Y + 0.9798Z = 6.790
Benzene _{1A}	0.1454X - 0.0509Y + 0.9881Z = 7.724
Benzene _{2A}	-0.2180X + 0.2041Y + 0.9544Z = 8.456
Benzene _{3A}	0.2772X + 0.3127Y + 0.9085Z = 9.749
Benzene _{1B}	0.0342X + 0.3570Y + 0.9335Z = 7.588
Benzene _{2B}	-0.0985X + 0.0256Y + 0.9948Z = 5.667
Benzene _{3B}	0.3031X + 0.0570Y + 0.9513Z = 6.163

^a Based on the crystal coordinate system, but in ångströms rather than fractional coordinates.

away from each other at the perimeter of the complex with an average angle between benzene pairs of 15°.

The benzene rings occur as three closely interacting pairs with a mean interplanar spacing³³ of 3.2 Å and closest C-C contacts between TRI ligands averaging 2.9 Å. In contrast the interplanar distance in crystalline perylene³⁴ is 3.46 Å, while that in perylene-pyromellitic dianhydride³⁵ (a tight donor-acceptor complex) is 3.23 Å. Furthermore, the direction of the torsional distortion about the molecular threefold axis (*vide supra*) is in a direction leading to increased overlap of the benzene pairs (while the distance between the benzene groups is increased). This, along with the preferential tendency²³ to form the racemic form, **5**, rather than the *meso* form, **6** (which would minimize contacts between the benzene groups), leads to the conclusion that the in-



teraction between the TRI ligands is attractive rather than repulsive. Consequently it is surprising that attempts to separate the racemates of Ni(TRI)₂²⁺ by chromatographic techniques have not been successful, leading Taylor and Busch³⁶ to propose a *meso* structure for this ion. It is hoped that further structural investigations in progress will clarify this question.

An examination of interatomic distances in the unit cell indicated a O₂-O₃ distance of 2.87 Å, possibly indicative of hydrogen bonding. The atom O₃ is located in a position nearly equidistant from the three nitrogen atoms of TRI ligand A, but the distances (3.26-3.36 Å) are sufficiently great to indicate that this can be attributed to packing rather than any type of bonded interaction. The contacts between I₁ and C_{27B} (3.44 Å) and between I₃ and O₂ (3.42 Å) are somewhat less than would normally be expected but not unreasonably so. All other contacts are greater than the sum of the corresponding van der Waals radii.

Interpretation of the Circular Dichroism Spectrum

A. The 4400-4900-Å Region. *The most striking feature of the circular dichroism curve of (+)₅₄₆₁-Co-*

(33) Defined as the distance from the center of gravity of one benzene group to the best plane for the adjacent benzene group.

(34) A. Camerman and J. Trotter, *Proc. Roy. Soc., Ser. A*, **279**, 129 (1964).

(35) J. C. A. Boyens and F. H. Herbststein, *J. Phys. Chem.*, **69**, 2160 (1965).

(36) L. T. Taylor and D. H. Busch, *Inorg. Chem.*, **8**, 1366 (1969).

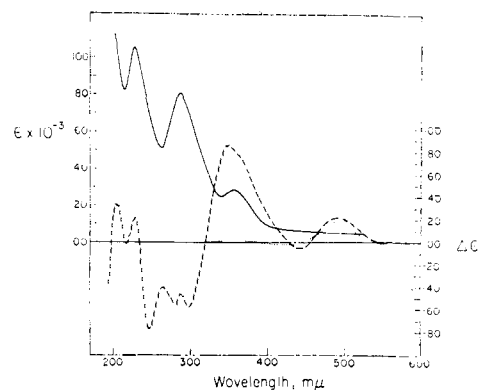


Figure 3. Electronic (—) and CD (----) curves for (+)₅₄₆₁-Co(TRI)₂³⁺ and the CD (.....) curve (×10) for (+)₅₄₆₁-Co(en)₃³⁺.

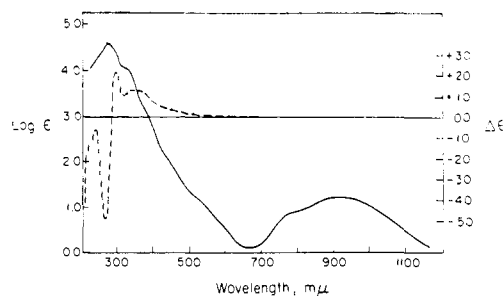


Figure 4. Electronic (—) and CD (----) curves for (+)₅₄₆₁-Ni(TRI)(H₂O)₃²⁺.

(TRI)₂³⁺²³ is its similarity to that for (+)₅₄₆₁-Co(en)₃³⁺ (Figure 3) in the 4700-Å region. In the case of the latter system the two low-energy transitions (trigonal components of ¹T_{1g} ← ¹A_{1g}) have been assigned as ¹E_a ← ¹A₁ and ¹A₂ ← ¹A₁ by Ballard, McCaffery, and Mason¹⁶ on the basis of their very comprehensive single-crystal CD studies. Further it is generally accepted that the relative signs of the two components of this trigonally split transition serve to fix the absolute configuration of cobalt(III) complexes. Since the absolute configuration of (+)₅₄₆₁-Co(en)₃³⁺ is known to be Λ(C₃),¹⁴ (+)₅₄₆₁-Co(TRI)₂³⁺ is expected to be Λ as well.³⁷

It is important to point out two structural features inherent in the TRI ligand which could in principle be the source of the metal-centered (*i.e.*, d-d transitions) optical activity. These are, respectively, the pitch of the benzene rings and the chirality in the arrangement of the C=N double bonds. The only indication we have of the importance of such vicinal effects³⁸ is derived from the electronic and CD spectra of (+)₅₄₆₁-Ni(TRI)(H₂O)₃²⁺³⁹ (Figure 4). Although there are several metal-centered transitions which are both electric and magnetic dipole allowed between 500 and 900 mμ, the first CD maximum occurs at *ca.* 360 mμ. Thus we are forced to conclude that *one TRI ligand was ineffective at putting the nickel chromophore in a dissymmetric environment.*⁴⁰

(37) See *ibid.*, **9**, 1 (1970), for nomenclature.

(38) C. T. Liu and B. E. Douglas, *ibid.*, **3**, 1356 (1964), and references therein.

(39) L. T. Taylor and D. H. Busch, *J. Amer. Chem. Soc.*, **89**, 5372 (1967).

(40) Note: although the ³E_b ← ³A₁ transition is allowed in the CD according to symmetry selection rules, its rotatory strength is weaker by a factor of ~10 than expected for the ³E_a ← ³A₁ transition, which could not be observed due to instrumental limitations. The lack of an

Of all the models and theories of optical activity in trigonal systems, only the one put forward by Piper and Karipides³ simply and correctly relates the known absolute configurations of (+)₅₄₆₁-Co(TRI)₂³⁺ and (+)₅₄₆₁-Co(en)₃³⁺. The essential feature of this model is the production of a twisted ligand field around the metal *via* a torsion of the metal complex about its threefold axis. The sense of the field determines the sign of optical rotation for a given transition. Indeed, it is our finding that the sense of the twisted ligand field is $\Lambda(C_3)$ for both (+)₅₄₆₁-Co(TRI)₂³⁺ and (+)₅₄₆₁-Co(en)₃³⁺.^{41, 42}

B. 3200–4000-Å Region. The ${}^1T_{2g} \leftarrow {}^1A_{1g}$ transition which is split in the trigonal limit into two components (${}^1E \leftarrow {}^1A_1$, and ${}^1A_1 \leftarrow {}^1A_1$) is expected in this region. Since the latter of these two components is electric and magnetic dipole forbidden, only one band should be observed. However, we observe a very strong band ($\Delta\epsilon = +85$) at 3480 Å and a well-defined long wavelength shoulder at *ca.* 3700 Å, which has $\Delta\epsilon \sim 20$ when a gaussian corresponding to the intense band is subtracted out. We feel that the 3480-Å band is due to charge transfer (ϵ 32,000³) and the ${}^1E \leftarrow {}^1A_1$ transition occurs at 3700 Å. Based on the proposed assignments for ${}^1T_{1g} \leftarrow {}^1A_1$ and ${}^1T_{2g} \leftarrow {}^1A_1$ we find $10Dq \approx 28,000 \text{ cm}^{-1}$, which places TRI close to bipyridyl in the spectrochemical series.⁴³

C. 2000–3200-Å Region. We stand to learn much about the complex if the benzene $\pi^* \leftarrow \pi$ transition expected in this energy range can be assigned.

As a guide we refer to the Ni(TRI)(H₂O)₃²⁺ spectra³⁹ (Figure 4). We note a strong maximum in the electronic spectrum and a corresponding strong negative CD band at 2700 Å. This is the proper region for the benzene $\pi^* \leftarrow \pi$ transition, and the large molar extinction coefficient (42,000) along with the small *g* value⁴⁴ ($\Delta\epsilon/\epsilon \sim 0.001$) support our argument for that assignment.

We see in the spectrum of Co(TRI)₂³⁺ an absorption at 2875 Å having a molar extinction coefficient of 80,000, or nearly twice that for the nickel complex which contains only one TRI ligand. This is satisfying, since one might expect additivity of intensity for a truly ligand-based transition, given that the electric dipole operators are parallel, which is most certainly true in this case. When we direct our attention to the CD curve for Co(TRI)₂³⁺ we find no band at 2875 Å, but rather two bands, one at 2990 Å and the other at 2780 Å. Further, we see that $\Delta\epsilon$ for each is ~ -50.0 , which is the same as the $\Delta\epsilon$ value observed in Ni(TRI)(H₂O)₃²⁺.

ORD tail, however, leads us to believe the latter also has zero rotatory strength.

(41) We find that (–)₅₄₆₁-Co(EDTA)^{2–}, which has been assigned the Λ configuration (B. E. Douglas, R. A. Haines, and J. G. Brushmiller, *Inorg. Chem.*, **2**, 1194 (1963), and references therein), suffers from a $\Delta(C_3)$ and the less obvious but definite $\Lambda(C_3)$ distortion within the immediate coordination sphere: H. A. Weakliem and J. L. Hoard, *J. Amer. Chem. Soc.*, **81**, 549 (1959).

(42) We note that the nickel coordination sphere in Ni(TRI)(H₂O)₃(NO₂)₂²⁺ has C_{3v} symmetry, and is a trigonal antiprism if one does not distinguish between O and N.

(43) B. N. Figgis, "Introduction to Ligand Fields," Interscience Publishers, New York, N. Y., 1966.

(44) S. F. Mason, *Proc. Chem. Soc.*, 137 (1962).

The red shift and resultant 1,400-cm^{–1} splitting between the symmetric and antisymmetric benzene π states^{45, 46} (exciton splitting) is a further indication of the strong interaction between benzene pairs.

On the assumption that the $\pi^* \leftarrow \pi$ transition *vide supra* has been correctly assigned, and that the resultant optical rotation is best described by the dipole-coupling mechanism,^{47, 48} it follows that the pitch of the benzene rings in (+)₅₄₆₁-Ni(TRI)(H₂O)₃²⁺ must have the sense of a left-handed screw.

Summary and Conclusions

We find strong evidence in the structures and CD spectra of (+)₅₄₆₁-Co(TRI)₂³⁺ and (+)₅₄₆₁-Co(en)₃³⁺ for the metal-centered optical activity arising from the extant twisted crystal fields, which were found to be left-handed in both cases. This is in accordance with a model proposed by Piper and Karipides.³ The empirical correlations^{8, 9} generally used to predict absolute configurations are expected to work only if limited to contracting ligands (*i.e.*, five-membered chelate rings). If larger, potentially angle-expanding rings are present, the ligand and crystal field helicities may well have different senses. The use of metal-centered transitions in predicting configurations is then clearly unsatisfactory.¹⁰ Beaumont and Gillard⁴⁹ have given evidence that one expanding ligand out of three can be tolerated, but the present authors feel that there is insufficient evidence available in support of this argument. It must be emphasized that the key factor controlling the rotatory strength of metal d–d transitions is not ring strain but rather the cumulative effect of individual distortions which may give rise to a twisted crystal field.

We concede, however, that the single-crystal CD spectra of (+)₅₄₆₁-Co(TRI)₂³⁺ and (–)₅₄₆₁-Co(tn)₃³⁺ must be studied if the picture is to be clarified.

Finally we have assigned the Λ configuration (the three benzene rings describing a left-handed propeller) to (+)₅₄₆₁-Ni(TRI)(H₂O)₃²⁺.

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(45) H. Suzuki, "Electronic Absorption Spectra and Geometry of Organic Molecules," Academic Press, New York, N. Y., 1967, pp 112–114.

(46) (a) D. J. Cram and H. Steinberg, *J. Amer. Chem. Soc.*, **73**, 569 (1951); (c) D. J. Cram, R. H. Bauer, N. L. Allinger, R. A. Reaver, W. J. Wechter, and E. Heilbronner, *ibid.*, **81**, 5977 (1959).

(47) J. A. Schellman, *Accounts Chem. Res.*, **1**, 144 (1968).

(48) For an alternative point of view, see B. Bosnich, *Inorg. Chem.*, **7**, 2379 (1968).

(49) A. G. Beaumont and R. D. Gillard, *Chem. Commun.*, 438 (1969).