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The Crystal Structure of a Four-Coordinate Metal Complex, Bis(*N*-*tert*-butylpyrrole-2-carboxaldimino)cobalt(II)[1]

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Received August 25, 1971

The molecular structure of bis(*N*-*tert*-butylpyrrole-2-carboxaldimino)cobalt(II) has been determined from three-dimensional single-crystal X-ray data. The compound crystallizes with four monomeric molecules in an orthorhombic unit cell of symmetry *Pbcn* and dimensions a = 17.20 (2), b = 7.18 (1), and c = 15.23 (2) Å. The structure was solved by heavy-atom techniques and refined by the full-matrix least-squares method to $R(F)$ = 0.071 and $R_w(F)$ = 0.063, based on 656 independent photographic data. The molecule possesses exact C_2 symmetry with the twofold axis passing through the cobalt atom. The structure may be described as tetrahedral in that the two five-membered chelating CoN_2C_2 rings are perpendicular to each other, with the dihedral angle between the plane defined by Co, N(1), and N(2) atoms and the plane defined by Co, N(1′), and N(2′) atoms being 89.6 (4)°. The significant deviation of the CoN_4 fragment from a regular tetrahedron is shown both by the Co–N(pyrrole) bond length of 1.981 (7) Å, which is 0.085 Å shorter than the Co–N(azomethine) bond length of 2.066 (8) Å, and by the smaller intrachelate N–Co–N angle of 83.5 (3)° compared to the interchelate N–Co–N angles of range 121.8 (4)–126.2 (5)°. The N···N "bite" distance in the five-membered ring is 2.70 (1) Å. The pyrrole-2-carboxaldimine ligand is essentially planar. The N-substituted *tert*-butyl group is oriented such that the three methyl carbon atoms are in near-staggered positions with respect to the azomethine carbon atom. The analogous zinc(II) complex is presumably isostructural with the cobalt complex.

Introduction

It has long been known that bis-bidentate metal complexes can be derived from Schiff bases. Due to the great synthetic flexibility of Schiff base formations, numerous complexes have been prepared with a variety of different combinations of basic ligands and permutable metals.[3] Existence of these four-coordinated metal complexes either as planar, as tetrahedral, or as an intermediate configuration has been attributed to the strength and symmetry of the ligand field associated with the inherent tendency for a metal atom to form an energetically most stable configuration. In addition, steric hindrances in the molecule resulting from interaction of a functional group with the adjoining atoms also strongly influence the extent of distortion from one form to another. It is of interest, therefore, to study the ligand dependence of the change for the metal environment and the general trend of the metal in an isosteric ligand field to counterbalance the steric stress imposed on the molecule.

Structures of the complexes $(OC_6H_4CHNR)_2M$ (where R = OH, CH_3, C_2H_5, i-C_3H_7, *tert*-C_4H_9, C_6H_5) containing functionally substituted derivatives of the salicylaldimine HOC_6H_4CHNR, coordinated to the first-row transition metal(II), Ni^{2+} and Cu^{2+} in particular, have been well characterized by two- or three-dimensional X-ray data[3b] in terms of quantitative conformational change of four ligand sites with respect to the metal atom. In most cases, these structural investigations showed that the metal atom forms either a trans-planar or a distorted tetrahedral configuration. In contrast, relatively few structures of metal complexes involving basic ligands other than those derived from salicylaldimine as the Schiff base have been determined from X-ray diffraction measurements.

In 1966, Holm and his coworkers[4] synthesized and made extensive investigations of the chemistry and configurational equilibrium of bis(pyrrole-2-carboxaldimino)metal(II) complexes in solution by means of magnetic susceptibility, electronic spectroscopy, and nmr spectroscopy. From the many bis(*N*-alkylpyrrole-2-carboxaldimino)metal(II)[1c] derivatives utilized in their studies,[5] we chose for a systematic X-ray investigation a series of bis-bidentate complexes, bis(*N*-*tert*-butylpyrrole-2-carboxaldimino)metal(II), where M = Co, Ni, Cu, and Zn. Of particular interest was the effect of bulky branched *tert*-butyl groups attached to azomethine nitrogen atoms upon the coordination of the these ligands to the metal atom. Details of our investigations provide an inclusive comparison of the molecular architectures for these four analogous metal complexes. Furthermore, these complexes are of biological interest, inasmuch as the pyrrole-2-carboxaldimine ligand is an isosteric fragment of pyrromethenes and porphyrins. The stereochemistry of the cobalt complex is presented here. A preliminary account of the structures has been given by Holm, *et al.*[4]

Experimental Section

Black platelike crystals of $(C_9H_{13}N_2)_2Co^{II}$, kindly made available by Professor R. H. Holm at the University of Wisconsin (now at Massachusetts Institute of Technology), were recrystallized from an n-heptane solution. A single crystal with dimensions 0.17 × 0.43 × 0.62 mm was mounted inside a thin-walled glass capillary with the 0.62-mm direction (corresponding to the c rotation axis) along the capillary axis. Multiple-film equiinclination Weissenberg data ($hk0$–$hk15$) and multiple-exposure precession data ($h0l$ and $h1l$) were obtained with Zr-filtered Mo Kα radiation (λ 0.7107 Å). The crystal was found to be stable to the X-radiation. Unit cell parameters were determined from precession photographs. Intensities were estimated visually by comparison with corresponding sets of standard spots and then corrected for Lorentz and polarization effects.

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[1] (a) Research jointly supported by the Wisconsin Alumni Research Foundation at the University of Wisconsin and by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp. (b) Presented in part at the Winter Meeting of the American Crystallographic Association, Tulane University, New Orleans, La., March 1–5, 1970. (c) Chemical Abstracts uses the systematic name 2-(*N*-*tert*-butylformimidoyl)pyrrole for the organic moiety of this compound.

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[3] (a) R. H. Holm, G. W. Everett, Jr., and A. Chakravorty, *Progr. Inorg. Chem.*, **7**, 83 (1966); (b) references cited in ref 3a.

[4] R. H. Holm, A. Chakravorty, and L. J. Theriot, *Inorg. Chem.*, **5**, 625 (1966).

[5] Metal complexes include R = CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9, *sec*-C_4H_9, *tert*-C_4H_9, $CH(C_2H_5)_2$, $CH_2CHCH_2OCH_3$, C_6H_{11}, $CH_3CHCH(CH_3)_2$, p-$C_6H_4CH_3$; M = Co, Ni, Cu, Zn, Pd.

Corrections for spot extension[6] were applied to the Weissenberg data. No corrections were made for extinction or absorption. With the linear absorption coefficient having a μ value of 9.2 cm^{-1} for Mo Kα radiation, the maximum intensity variation on a given layer due to absorption was estimated to be less than 10%. Reflections appearing in both Weissenberg and precession photographs were used to assign initial individual relative scale factors for the 18 reciprocal levels; these separate reciprocal-level scale factors were subsequently varied in the least-squares refinement. A total of 656 independent, observed diffraction maxima, of which 616 reflections were recorded from Weissenberg data and an additional 40 reflections were recorded from precession data, were used throughout this investigation. Minimum observed intensities, I_o (min), were estimated for each reciprocal level, and variable weights for the observed structure amplitudes, F_o, were assigned in the following way: $\sqrt{w} = 20/F_o$ if $I_o \geq 4I_o$ (min); $\sqrt{w} = 1.25I_o{}^2/F_o[I_o\ (\mathrm{min})]^2$ if $I_o < 4I_o$ (min).

Crystal Data

Crystals of $(C_9H_{13}N_2)_2Co^{II}$ (mol wt 357.38) are orthorhombic with $a = 17.20$ (2), $b = 7.18$ (1), and $c = 15.23$ (2) Å (lattice parameter errors were estimated on the basis of reproducibility of the measurements). The volume of the unit cell is 1881 Å^3. The observed density of 1.23 (2) g cm^{-3} (obtained by flotation) is close to the calculated value of 1.26 g cm^{-3} based on four formula species of $(C_9H_{13}N_2)_2Co$ in a unit cell. The total number of electrons per cell, $F(000)$, is 756. Systematic absences of $0kl$ for k odd, $h0l$ for l odd, and $hk0$ for $h + k$ odd are uniquely characteristic of the space group $Pbcn$ ($D_{2h}{}^{14}$, no. 60);[7] this centric space group, subsequently confirmed by a satisfactory refinement of the structure, required (in the absence of any order–disorder phenomena) that each of the four $(C_9H_{13}N_2)_2Co$ molecules be located on either a twofold axis or a center of symmetry.

Determination of the Structure

The location of the crystallographically independent cobalt atom on the twofold axis passing through $x = 0$ and $z = {}^1/_4$ (corresponding to the four cobalt atoms per cell occupying the special fourfold set of positions (4c): $0, y, {}^1/_4;\ 0, -y, {}^3/_4;\ {}^1/_2, {}^1/_2 + y, {}^1/_4;\ {}^1/_2, {}^1/_2 - y, {}^3/_4$)[7] was inferred both from the dominant number of hkl reflections with $h + k$ even (532 out of the 656 total observed reflections, corresponding to approximately 81% of the data) and from the greater intensities of the hkl reflections with $h + k$ even.

A three-dimensional sharpened Patterson function, computed by the Blount program,[8] with $|F_o|^2[\Sigma Z_j/\Sigma f_j]^2$ as coefficients,[9] provided an initial y coordinate for the independent cobalt atom. This parameter and an assumed isotropic temperature factor for the cobalt atom were refined by the least-squares program[10] for the reflections with $h + k$ even[11] to give an unweighted reliability index, $R(F) = \Sigma||F_o| - s|F_c||/\Sigma|F_o|$, where s is the adjusted scale factor, of 0.31. A three-dimensional Fourier synthesis phased on the resulting refined parameters was next calculated[8] for the reflections with $h + k$ even. Since the presence of cobalt atoms on the assigned special positions necessarily generates pseudocenters of symmetry at $\pm({}^1/_4, {}^1/_4, 0;\ {}^1/_4, {}^3/_4, 0;\ {}^1/_4, {}^1/_4, {}^1/_2;\ {}^1/_4, {}^3/_4, {}^1/_2)$, the phase contributions of the cobalt atoms to the structure factors are such as to result in a superposition of Fourier peaks for two structures—the partially correct structure and its false image. Initial positions for carbon and nitrogen atoms were chosen based upon *a priori* chemical grounds, and all 11 nonhydrogen light atoms in the asymmetric unit were subsequently found. Each of these atoms is located on the eightfold set of general positions (8d): $\pm(x, y, z;\ {}^1/_2 - x, {}^1/_2 - y, {}^1/_2 + z;\ {}^1/_2 + x, {}^1/_2 - y, -z;\ -x, y, {}^1/_2 - z)$.[7] Nine cycles of isotropic least-squares refinement,[10] in which all reflections (*i.e.*, those with $h + k$ both even and odd) were included, converged slowly to give an $R(F)$ value of 0.093 and a weighted reliability index, $R_w(F) = [\Sigma w||F_o| - s|F_c||^2/\Sigma w|F_o|^2]^{1/2}$, of 0.098. At the end of this refinement, the isotropic temperature factors of carbon atoms ranged from 3.6 Å^2 for C(6) to 7.8 Å^2 for C(2), while all parameter shifts were less than 2% of the corresponding standard deviations. The 18 reciprocal-layer scale factors (whose values ranged from 0.399 to 0.592 for the Weissenberg data and 0.131 and 0.139 for the precession data) obtained from the isotropic refinement were used to place all of the observed structure amplitudes on a single relative scale. A full-matrix anisotropic refinement[10] with one variable scale factor was then performed until changes of individual parameters again became negligible with respect to the corresponding standard deviations. After four cycles, $R(F)$ and $R_w(F)$ dropped to 0.086 and 0.083, respectively. A difference Fourier synthesis calculated[8] at this stage showed two positive peaks of densities of 0.6 and 0.9 e/Å^3 in the neighborhood of the cobalt atom with the remaining positive peaks ranging from 0.2 to 0.5 e/Å^3 (equivalent to approximately 5–11% of the average Fourier peak intensity for the nine carbon atoms). The minimum density on the map was −0.4 e/Å^3. All 13 independent hydrogen atoms were located from this map. Since an attempt to refine the positional parameters of these hydrogen atoms (with a reasonable fixed isotropic temperature factor of 7.0 Å^2 being assigned to each atom) together with the positional and anisotropic thermal parameters for the nonhydrogen atoms did not converge, the positional parameters of the 13 hydrogen atoms as well as their assigned isotropic temperature factors were fixed in the final refinement. After four cycles, the $R(F)$ and $R_w(F)$ values remained at 0.071 and 0.063, respectively. The parameter shifts were all less than 0.3% of the corresponding standard deviations. All least-squares refinements were based on the minimization of $\Sigma w||F_o| - s|F_c||^2$, and the standard errors $\sigma(F_o)$ of the observation were related to the previously defined w values by the relation $\sigma(F_o) = 1/\sqrt{w}$. The final standard deviation of an observation of unit weight—defined as $[\Sigma w||F_o| - s|F_c||^2/(n - p)]^{1/2}$, where n is the number of observations and p the number of parameters fitted to the data set—is 0.986. The atomic scattering factors used were those of Thomas and Umeda[12] for cobalt, those of Berghuis, *et al.*,[13] for carbon and nitrogen, and those tabulated by Ibers[14] for hydrogen. The constants[15] $\Delta f' = 0.4$ and $\Delta f'' = 1.1$ were employed in the correction of the calculated structure factors for the anomalous scattering of the cobalt atoms. The final parameters with estimated standard deviations, obtained from the output of the last cycle of the refinement, are given in Table I. Observed and calculated structure amplitudes are available as indicated in ref 16. Interatomic distances and angles and their estimated standard deviations, calculated with the Busing–Martin–Levy program[17] from the full inverse matrix (containing estimated lattice parameter errors), are presented in Tables II and III, respectively. The root-mean-square thermal displacements along the directions of the principal axes are given for the nonhydrogen atoms in Table IV. "Best" molecular planes formed by sets of specified atoms and perpendicular distances of these and other atoms from these planes were calculated by a weighted least-squares method.[18] All figures were prepared by the use of the Johnson program.[19]

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(6) D. C. Phillips, *Acta Crystallogr.*, **7**, 746 (1954).

(7) "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1965, p 149.

(8) J. F. Blount, Ph.D. Thesis (Appendix), University of Wisconsin, Madison, Wis., 1965.

(9) See, *e.g.*, H. Lipson and W. Cochran, "The Determination of Crystal Structures," G. Bell and Sons, London, 1957, p 170.

(10) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, A Fortran Crystallographic Least-Squares Program," Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(11) Inasmuch as cobalt atoms are positioned at the (4c) special positions and only cobalt atoms are considered in the unit cell, their contribution to the structure factors is such that it results in nonzero values only for the reflections with $h + k$ even as in the case of C-centering structures.

(12) L. H. Thomas and K. Umeda, *J. Chem. Phys.*, **26**, 293 (1957).

(13) J. Berghuis, I. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenendaal, *Acta Crystallogr.*, **8**, 478 (1955).

(14) J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 202, Table 3.3.1A.

(15) (a) C. H. Dauben and D. H. Templeton, *Acta Crystallogr.*, **8**, 841 (1955); (b) D. H. Templeton, "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 215, Table 3.3.2C.

(16) A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-1100. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(17) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, A Fortran Crystallographic Function and Error Program," Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

(18) D. L. Smith, Ph.D. Thesis (Appendix IV), University of Wisconsin, Madison, Wis., 1962.

(19) C. K. Johnson, "A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustration," Report ORNL-3794, 2nd revision, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1970.

TABLE I

POSITIONAL AND THERMAL PARAMETERS ($\times 10^4$) FOR $(C_9H_{13}N_2)_2Co^{II}$ [a,b]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	0	0.2213 (2)	$^1/_4$	32 (1)	180 (4)	43 (1)	0	−2 (1)	0
N(1)	0.1023 (5)	0.0815 (10)	0.2236 (4)	37 (3)	221 (20)	35 (4)	−0.6 (7)	−6 (3)	1 (6)
N(2)	0.0634 (5)	0.3461 (11)	0.3413 (4)	32 (4)	205 (20)	42 (4)	16 (7)	0.1 (3)	−5 (7)
C(1)	0.1171 (6)	−0.0650 (14)	0.1563 (5)	38 (5)	221 (26)	41 (4)	6 (9)	−1 (4)	−8 (10)
C(2)	0.1968 (8)	−0.0300 (15)	0.1141 (7)	68 (7)	345 (33)	82 (7)	−15 (13)	33 (6)	−58 (12)
C(3)	0.0549 (9)	−0.0531 (16)	0.0888 (7)	93 (8)	302 (36)	66 (6)	45 (13)	−15 (7)	−22 (12)
C(4)	0.1155 (7)	−0.2541 (14)	0.2033 (8)	63 (5)	220 (28)	76 (5)	10 (10)	−5 (5)	−12 (12)
C(5)	0.1553 (6)	0.1378 (15)	0.2755 (6)	32 (4)	271 (26)	54 (7)	−10 (9)	9 (4)	−3 (9)
C(6)	0.1376 (6)	0.2798 (13)	0.3397 (5)	42 (5)	189 (25)	32 (4)	−19 (10)	−0.4 (3)	−6 (8)
C(7)	0.1836 (6)	0.3638 (16)	0.4021 (6)	60 (6)	254 (26)	39 (5)	−9 (12)	−6 (4)	−5 (9)
C(8)	0.1357 (7)	0.4922 (15)	0.4441 (7)	77 (7)	287 (29)	46 (5)	−28 (14)	−7 (6)	−20 (10)
C(9)	0.0612 (7)	0.4794 (14)	0.4059 (6)	53 (6)	211 (28)	42 (5)	−3 (10)	−9 (5)	5 (9)
H(2a)	0.2091	−0.1443	0.0675	*c*					
H(2b)	0.1972	0.1128	0.0806	*c*					
H(2c)	0.2333	−0.0777	0.1628	*c*					
H(3a)	0.0814	−0.1667	0.0371	*c*					
H(3b)	0.0064	−0.0693	0.1145	*c*					
H(3c)	0.0490	0.0568	0.0564	*c*					
H(4a)	0.1278	−0.3502	0.1482	*c*					
H(4b)	0.1601	−0.2645	0.2519	*c*					
H(4c)	0.0715	−0.2546	0.2423	*c*					
H(5)	0.2119	0.0989	0.2672	*c*					
H(7)	0.2432	0.3405	0.4250	*c*					
H(8)	0.1431	0.5826	0.4934	*c*					
H(9)	−0.0035	0.5361	0.4028	*c*					

[a] Least-squares derived standard deviations of the least significant figures are given in parentheses in all tables and in the text. Since no absorption corrections were applied, these values represent a lower limit for the true standard deviations. See W. C. Hamilton and S. C. Abrahams, *Acta Crystallogr., Sect. A*, **26**, 18 (1970). [b] The form of the anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [c] Hydrogen atoms were assigned isotropic temperature factors of 7.0 Å^2.

TABLE II

INTERATOMIC DISTANCES (Å)[a]

Co–N(1)	2.066 (8)	C(2)···C(3)	2.47 (2)
Co–N(2)	1.981 (7)	C(3)···C(4)	2.49 (2)
N(1)–C(1)	1.49 (1)	C(4)···C(2)	2.53 (2)
N(1)–C(5)	1.27 (1)		
C(5)–C(6)	1.44 (1)	C(5)–H(5)	1.02
C(6)–C(7)	1.38 (1)	C(7)–H(7)	1.10
C(7)–C(8)	1.39 (1)	C(8)–H(8)	1.00
C(8)–C(9)	1.41 (1)	C(9)–H(9)	1.19
N(2)–C(9)	1.37 (1)	C(2)–H(2a)	1.11
N(2)–C(6)	1.36 (1)	C(2)–H(2b)	1.15
C(1)–C(2)	1.53 (2)	C(2)–H(2c)	1.03
C(1)–C(3)	1.49 (1)	C(3)–H(3a)	1.22
C(1)–C(4)	1.54 (1)	C(3)–H(3b)	0.93
		C(3)–H(3c)	0.94
N(1)···N(2)	2.70 (1)	C(4)–H(4a)	1.11
N(1)···N(1′)	3.61 (2)	C(4)–H(4b)	1.07
N(1)···N(2′)	3.57 (1)	C(4)–H(4c)	0.96
N(2)···N(2′)	3.53 (1)	Mean C–H	1.06

[a] Primes refer to atoms related to those in the asymmetric unit by the crystallographic twofold axis.

TABLE III

INTRAMOLECULAR ANGLES (DEG) WITH STANDARD DEVIATIONS[a]

N(1)–Co–N(2)	83.5 (3)	Co–N(2)–C(9)	143.4 (7)
N(1)–Co–N(1′)	121.8 (4)	C(5)–C(6)–C(7)	130.9 (7)
N(1)–Co–N(2′)	123.5 (3)	Co–N(1)–C(1)	128.5 (6)
N(2)–Co–N(2′)	126.2 (5)	C(5)–N(1)–C(1)	122.0 (8)
Co–N(1)–C(5)	109.6 (6)	N(1)–C(1)–C(2)	109.0 (8)
Co–N(2)–C(6)	110.2 (5)	N(1)–C(1)–C(3)	108.2 (8)
N(1)–C(5)–C(6)	119.6 (9)	N(1)–C(1)–C(4)	107.5 (7)
N(2)–C(6)–C(5)	117.2 (8)	C(2)–C(1)–C(3)	110.1 (9)
C(6)–N(2)–C(9)	106.4 (8)	C(3)–C(1)–C(4)	111.1 (9)
N(2)–C(6)–C(7)	111.9 (8)	C(4)–C(1)–C(2)	110.9 (9)
N(2)–C(9)–C(8)	108.5 (9)	C(2)–C(3)–C(4)	61.2 (5)
C(6)–C(7)–C(8)	105.5 (9)	C(3)–C(4)–C(2)	59.1 (5)
C(9)–C(8)–C(7)	107.7 (9)	C(4)–C(2)–C(3)	59.7 (5)

[a] Primes refer to atoms related to those in the asymmetric unit by the crystallographic twofold axis.

TABLE IV

ROOT-MEAN-SQUARE THERMAL DISPLACEMENTS ALONG THE DIRECTIONS OF THE PRINCIPAL AXES (IN Å)

Atom	Axis 1	Axis 2	Axis 3
Co	0.214 (4)	0.217 (3)	0.229 (3)
N(1)	0.194 (12)	0.239 (11)	0.242 (11)
N(2)	0.201 (14)	0.222 (11)	0.248 (11)
C(1)	0.215 (13)	0.233 (15)	0.250 (15)
C(2)	0.217 (16)	0.292 (16)	0.394 (16)
C(3)	0.256 (15)	0.271 (16)	0.397 (16)
C(4)	0.235 (15)	0.290 (12)	0.317 (14)
C(5)	0.202 (14)	0.257 (14)	0.275 (12)
C(6)	0.189 (14)	0.210 (15)	0.264 (16)
C(7)	0.210 (13)	0.257 (13)	0.304 (16)
C(8)	0.214 (15)	0.277 (14)	0.349 (16)
C(9)	0.212 (13)	0.235 (16)	0.289 (14)

Discussion

The crystal structure of $(C_9H_{13}N_2)_2Co^{II}$ is composed of molecules with the configuration depicted in Figure 1. The cobalt atom is coordinated to two bidentate ligands of N-substituted pyrrole-2-carboxaldimine, so that the configuration around the metal atom is tetrahedral-like. A projection of the molecule in the [010] direction is given in Figure 2, where bond distances for the molecule and bond angles for the CoN_4 moiety are also given.

As in the case of bis(*N*-isopropyl-3-ethylsalicylaldiminato)nickel,[20] the dihedral angle between the coordination plane defined by atoms M, N(1), and N(2) and the coordination plane defined by atoms M, N(1′), and N(2′) (prime atoms are those related to the corresponding basic atoms by the crystallographic twofold axis) can be taken as a measure of the degree of distortion from regularity of the coordination tetrahedron. The calculated value of 89.6 (4)° for $(C_9H_{13}N_2)_2Co^{II}$ shows that the two bidentate ligands are experimentally perpendicular to each other. Although the arrangement of the four nitrogen atoms about the Co(II) may be considered to correspond to a tetra-

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(20) R. L. Braun and E. C. Lingafelter, *Acta Crystallogr.*, **22**, 780 (1967).

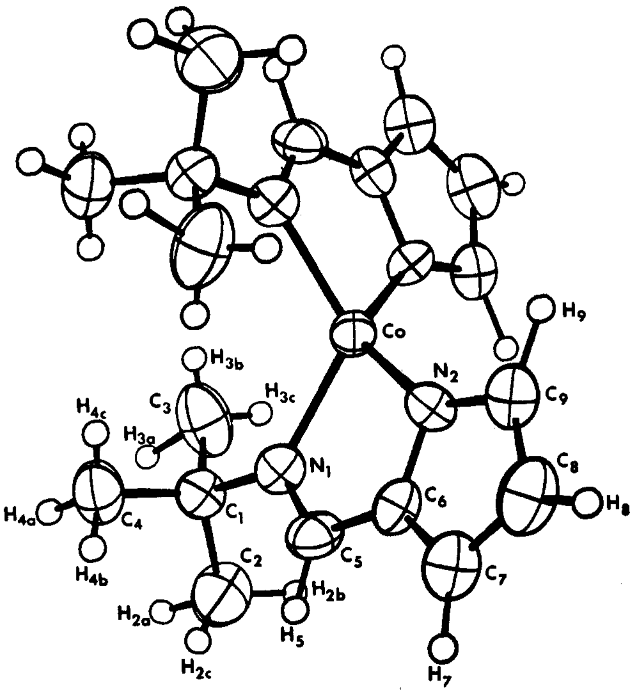

Figure 1.—Molecular configuration with C_2 symmetry. A crystallographic twofold axis passes through the cobalt atom and relates the remaining parts of the molecule in pairs. Nonhydrogen atoms are shown as 50% probability thermal ellipsoids.[19]

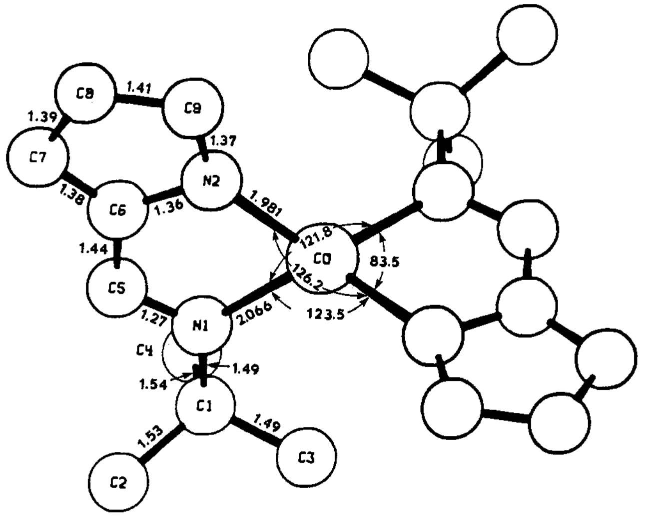

Figure 2.—[010] projection of the molecule corresponding to the view along the crystallographic twofold axis passing through the cobalt atom. For clarity, hydrogen atoms are not included.

hedral geometry[21–28] deduced from the observed magnetic moment of 4.67 BM in the solid state,[4] the MN_4 tetrahedron is significantly elongated along the direction bisecting the chelating rings such that the acute *intrachelate* N(1)–Co–N(2) angle of 83.5 (3)° is appreciably smaller than the normal value of 109° 28′ for a regular tetrahedron and much smaller than the other three crystallographically independent *interchelate* angles of 121.8 (4), 123.5 (3), and 126.2 (5)° for N(1)–Co–N(1′), N(1)–Co–N(2′), and N(2)–Co–N(2′), respectively. These angular deviations may be attributed primarily to steric and electronic requirements of the bis-chelating ligands in their resulting linkages as five-membered CoN_2C_2 rings through the formation of M–N bonds. A significant bond-length deviation of the CoN_4 tetrahedron from regularity also occurs in that the Co–N(1) bond length of 2.066 (8) Å is 0.085 Å longer than the Co–N(2) bond length of 1.981 (7) Å. This large dissimilarity in M–N bond lengths, also observed in the analogous nickel(II)[29] and copper(II)[30] complexes, may be considered as a consequence of an unsymmetrical electron localization in the MN_4 system and may signify that the bonding between the metal atom and the deprotonated pyrrole-ring nitrogen atom is much stronger than that between the metal and the azomethine nitrogen atom.

It has been pointed out by several authors[31] that the mean metal–ligand bond energies increase slightly from cobalt to nickel in tetrahedral complexes. A comparison of M–N bond distances for the cobalt complex with those for the analogous pseudotetrahedral nickel complex[29] indeed reveals that the Co–N(1) and Co–N(2) bond distances are 0.034 and 0.046 Å longer than the corresponding values of 2.032 (4) and 1.935 (5) Å for Ni–N(1) and Ni–N(2), respectively.[32,33] Since the metallic radius of 1.162 Å for the cobalt atom is only 0.008 Å larger than that of 1.154 Å for the nickel atom,[34] the net increase in M–N bond

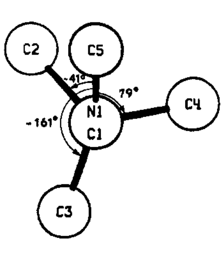

Figure 3.—View down the N(1)–C(1) bond direction showing the conformation of the *tert*-butyl group. The three methyl carbons are in nearly staggered positions relative to C(5).

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(21) Although a comprehsnsive study made by Holm and his coworkers[22] showed a planar–tetrahedral equilibrium in *solution* for four-coordinated bis(β-keto amino)cobalt(II) complexes, practically all four-coordinated nitrogen-donor Co(II) complexes, including bis(*N*-butylsalicylaldimino)-cobalt(II),[23] bis(*N*-R-salicylaldimino)cobalt(II) (where R = alkyl, aryl, cyclohexyl),[24] bis(*N*-isopropylsalicylaldimino)cobalt(II),[25] $(Et_4N)_2Co^{II}(NCO)_4$,[26] and a dipyrromethene complex of Co(II),[27] in the solid state, have been shown from powder, two-dimensional X-ray, magnetic, and spectrophotometric measurements to be tetrahedral, in accord with an inherent nature of the Co(II) ion to form more tetrahedral complexes than any other transition metal ion.[28] In the $(C_9H_{13}N_2)_2Co^{II}$ structure containing bulky *tert*-butyl groups attached to the azomethine nitrogen atoms, a trans-planar configuration would not be possible due to the resulting severe steric interactions which would arise between neighboring ligand atoms, particularly between H(9) and the *tert*-butyl group.[4]

(22) (a) G. W. Everett, Jr., and R. H. Holm, *J. Amer. Chem. Soc.*, **88**, 2442 (1966); (b) G. W. Everett, Jr., and R. H. Holm, *Inorg. Chem.*, **7**, 776 (1968).

(23) E. Frasson and C. Panattoni, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **116**, 154 (1961).

(24) L. Sacconi, M. Ciampolini, F. Maggio, and F. P. Cavasino, *J. Amer. Chem. Soc.*, **84**, 3246 (1962).

(25) L. Sacconi and P. L. Orioli, *Ric. Sci.*, **32**, 645 (1962).

(26) D. Forster and M. L. Goodgame, *J. Chem. Soc.*, 2790 (1964).

(27) J. E. Fergusson and C. A. Ramsay, *J. Chem. Soc.*, 5222 (1965).

(28) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience, New York, N. Y., 1966, p 865.

(29) C. H. Wei and J. R. Einstein, to be submitted for publication.

(30) C. H. Wei, to be submitted for publication.

(31) Reference 22b and references cited therein.

(32) A slightly larger range of 0.05–0.06 Å quoted by Everett and Holm[22b] for the difference in M–N bond distances for the tetrahedral cobalt and nickel complexes was based on a comparison of the X-ray results obtained from *photographic* data for the nickel complex.[33]

(33) C. H. Wei, unpublished work.

(34) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 256 or 403.

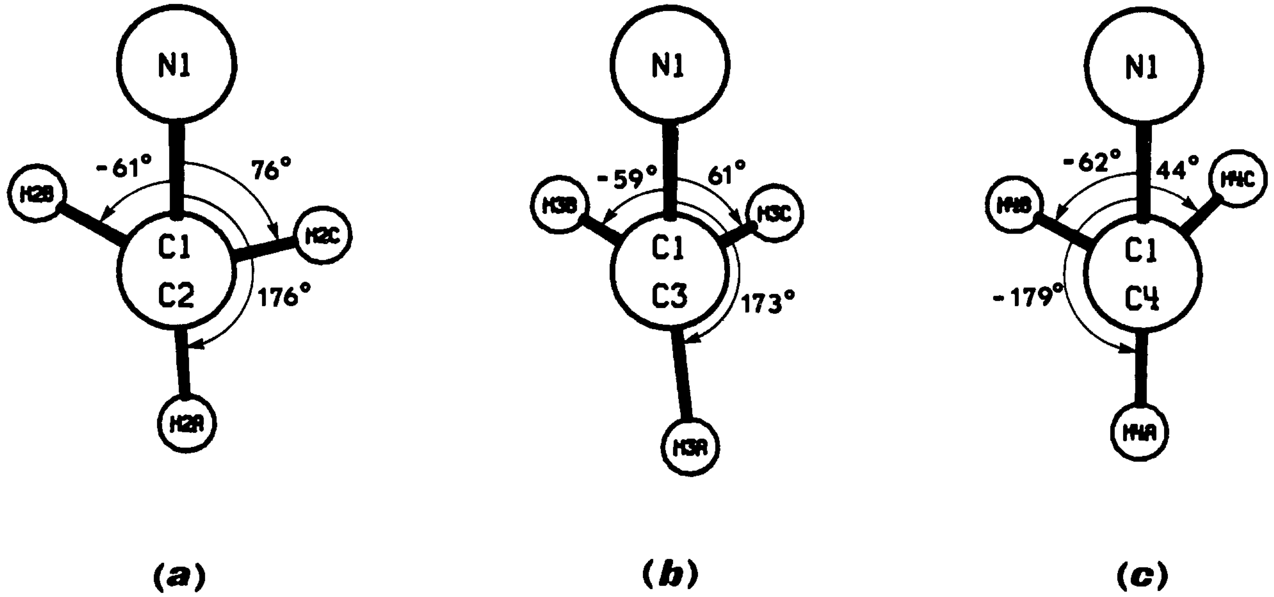

Figure 4.—Views down the three C(1)–CH_3 bond directions showing in each case that the hydrogen atoms are approximately in staggered positions relative to N(1).

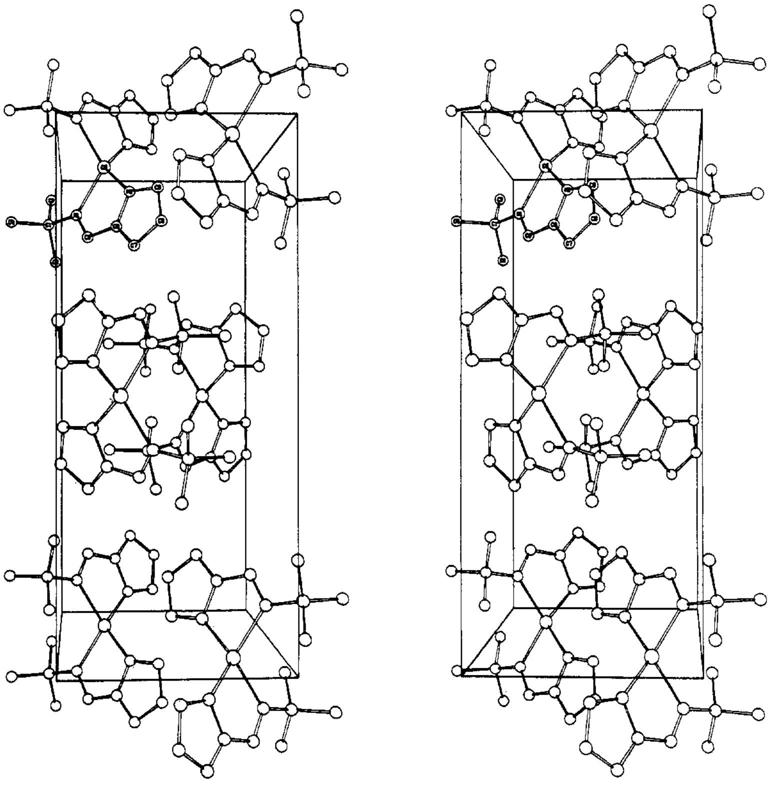

Figure 5. Stereoscopic view down the *c* axis of the unit cell. The origin of the unit cell is in the upper left rear corner and the *a* axis is downward. Only the basic atoms are labeled, and for clarity hydrogen atoms are omitted.

energies as the cobalt atom is replaced by the nickel atom in this type of tetrahedral complex is such as to result in a shortening of approximately 0.04 ± 0.006 Å in M–N lengths, inasmuch as bond lengths reflect bond energies.

The short N(1)–C(5) bond distance of 1.27 (1) Å in the azomethine group is compatible with the values obtained in the Schiff base–metal complexes bis(*N*-isopropyl-3-methylsalicylaldiminato)nickel(II) [1.287 (4) Å],[35] bis(*N*-isopropyl-3-ethylsalicylaldiminato)-nickel(II) [1.286 (3) Å],[36] bis(*N*-*tert*-isopropyl-3-ethylsalicylaldiminato)palladium(II) [1.286 (3) Å],[36] and bis(*N*-*tert*-butylsalicylaldiminato)copper(II) [1.25 (1) Å].[37] Examination of bond lengths and angles for the pyrrole ring in this structure shows that they parallel those of free pyrrole molecule.[38] Although the hydrogen parameters were not adjusted in the final least-

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(35) R. L. Braun and E. C. Lingafelter, *Acta Crystallogr.*, **21**, 546 (1966).

(36) R. L. Braun and E. C. Lingafelter, *ibid.*, **22**, 787 (1967).

(37) T. P. Cheeseman, D. Hall, and T. N. Waters, *J. Chem. Soc. A*, 685 (1966).

(38) "Tables of Interatomic Distances and Configuration in Molecules and Ions," The Chemical Society, London, 1965, p M108s.

squares refinement, the C–H bond distances ranging from 0.94 to 1.19 Å are not unlike others obtained by the X-ray diffraction method.

Calculation of a weighted best plane[18] passing through atoms of the pyrrole–C–NC–Co/2 moiety reveals that the constituent atoms are essentially coplanar. The maximum perpendicular displacement of individual atoms from this best plane is 0.013 Å for C(8), with the deviations of the remaining atoms ranging from −0.000 for Co to −0.008 Å for N(2).

A close conformability of the $N-C(CH_3)_3$ moiety to the tetrahedral geometry can be seen by an examination of the $N(1)-C(1)-CH_3$ angles, which vary from 107.5 (7) to 111.1 (9)° only. The *tert*-butyl group conformation may be described in a manner similar to that for peptide chain.[39] Figure 3 shows a view down the N(1)–C(1) bond. As expected, the three methyl carbons are roughly in staggered positions relative to C(5), the deviation from the ideal staggered conformation being a clockwise rotation of the methyl groups by 19° about the $N(1) \rightarrow C(1)$ axis. The arrangements of the methyl hydrogen atoms viewed down the C(1)–C(2), C(1)–C(3), and C(1)–C(4) bonds are shown in Figure 4. In each case, the three hydrogen atoms are in the expected staggered orientation relative to N(1).

Figure 5 shows the packing in a stereoscopic view down the *c* axis. While the shortest nonbonding intramolecular H···H distance [excluding those for H(methyl)···H(methyl)] is 2.07 Å for H(5)···H(2c), the closest intermolecular H···H contact is 2.38 Å for H(2a) and H(2b) of the adjacent molecule, thus indicating that no abnormal forces are responsible for the crystal packing.

Analogous cobalt and zinc complexes with tetrahedral chelates form isomorphous structures in a number of compounds involving bis(*N*-isopropylsalicylaldiminato)metal(II),[25,30] bis(*N*-butylsalicylaldiminato)metal(II),[23] bis(*N*-*sec*-butylsalicylaldiminato)metal(II),[40] $(Et_4N)_2M^{II}(NCO)_4$,[26] diethyl 3,3′,5,5′-tetramethyldipyrromethene-4,4′-dicarboxylate,[27] and diethyl 5′-bromo-3,4′,5-trimethyldipyrromethene-3′,4-dicarboxylate.[27] Single-crystal X-ray examination of bis(*N*-*tert*-butylpyrrole-2-carboxaldimino)zinc(II) reveals that the unit cell of the zinc complex is practically isodimensional with that of the analogous cobalt complex.[4] That these two complexes are rigorously isomorphous is further evidenced by their apparently indistinguishable intensity data.[33] Detailed comparison of structural characteristics of the series of $(C_9H_{13}N_2)_2M^{II}$ (M = Co, Ni, Cu) will be presented in a future paper.

Acknowledgments.—The author wishes to thank Professor R. H. Holm for furnishing a sample of the compound and for his interest in this work. Collection of the X-ray data was carried out at the University of Wisconsin in the laboratories of Professor L. F. Dahl, to whom the author is indebted for helpful discussions.

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[39] Several identical papers were published by the IUPAC–IUB Commission on Biochemical Nomenclature. As an example, see *Biochemistry*, **9**, 3471 (1970).

[40] L. Sacconi, P. L. Orioli, P. Paoletti, and M. Ciampolini, *Proc. Chem. Soc., London*, 255 (1962).

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The Crystal Structure of Hydridopentaamminerhodium(III) Perchlorate

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Received August 30, 1971

The crystal structure of hydridopentaamminerhodium(III) perchlorate, $[RhH(NH_3)_5][ClO_4]_2$, has been determined by X-ray diffractometric methods. The structure has been refined in the orthorhombic space group D_2^4-$P2_12_12_1$ with a = 10.2866 (12), b = 8.0689 (10), c = 15.0146 (21) Å, ρ_{obsd} = 2.07 (2) g/cm³, ρ_{calcd} = 2.07 g/cm³, and Z = 4, to a final conventional R factor of 0.040 for 1298 reflections above background. The compound consists of discrete octahedral hydridopentaamminerhodium(III) and tetrahedral perchlorate ions. The cations are stacked in zigzag chains of essentially linear Rh–H···N–Rh elements, whose Rh atoms are 6.103 (1) Å apart. The ammine group which is directed toward the next cation in the chain is the closest to the Rh atom, with an Rh–N distance of 2.048 (11) Å. The other three ammine groups cis to the H ligand have an average Rh–N distance of 2.079 (7) Å. The NH_3 which is trans to the H ligand is 2.244 (13) Å from the Rh, so that the H ligand is exerting a pronounced trans effect of 0.165 (15) Å. The Rh–H distance is 1.82 (17) Å.

Introduction

Although scores of structures of transition metal hydride complexes have been determined by diffraction methods, only four of these were carried out by neutron diffraction techniques where high accuracy in the placement of the hydride ligand is possible.[1] Neutron diffraction studies of transition metal hydrides are rare, not necessarily because of the limited availability of suitable facilities but more likely because of the unsuitability of most transition metal hydrides for such work. Many such complexes contain a large number of atoms since multiatom ligands, such as $P(C_6H_5)_3$, are used to stabilize them.

The present compound, hydridopentaamminerhodium(III) perchlorate, $[RhH(NH_3)_5][ClO_4]_2$, is an air-stable solid with a relatively small number of atoms. This present X-ray study was initiated in part to assess the crystallographic suitability of the complex for neutron diffraction investigation. This was done at a time when there was still considerable discussion about the

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[1] B. A. Frenz and J. A. Ibers in "Transition Metal Hydrides," E. L. Muetterties, Ed., Marcel Dekker, New York, N. Y., 1971, p 33.