The Crystal and Molecular Structure of Tris(π-cyclopentadienyl nickel)tertiary-butylammonium

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The crystal structure of tris(π-cyclopentadienylnickel)tertiary-butylammonium, t-$C_4H_9N(\pi$-$C_5H_5Ni)_3$, has been determined from single crystal X-ray diffractometer data. The space group is C2/c and the lattice constants are $a=28.40$ Å, $b=9.16$ Å, $c=15.28$ Å, $\beta=100°30'$, and $Z=8$. The refinement was carried out using block-diagonal least-squares calculation including anisotropic temperature factors for the three nickel atoms. The final R index for 1620 reflections is 0.138. The molecule is of approximately a trigonal pyramidal structure with an apical nitrogen atom on a triangle of the nickel atoms. The interatomic distances are 2.33—2.39 Å for nickel to nickel, 1.93—1.98 Å for nickel to nitrogen. The distances between a nickel atom and a centroid of a cyclopentadienyl ring are 1.74—1.81 Å. The three cyclopentadienyl rings are inclined to the nickel triangle plane at 68°—69°.

Tris(π-cyclopentadienylnickel)tertiary-butylammonium, t-$C_4H_9N(\pi$-$C_5H_5Ni)_3$, synthesized by a reaction of $(t$-$C_4H_9N)_2S$ with $(\pi$-$C_5H_5)_2Ni$ or with $(\pi$-$C_5H_5Ni(CO))_2$ in heptane solution, is reported to be paramagnetic (1.68 B.M., $g=2.035$).[1] IR, UV, and EPR spectra suggest that the molecule has a pyramidal structure with an apical nitrogen atom on a triangle of the nickel atoms.[1]

We have carried out a crystallographic study of the title substance in order to confirm the suggested structure, special attention being paid to the Ni-Ni distances because of their bondings including one unpaired electron.

Experimental

Crystals obtained from a heptane solution[1] were blue-black irregular platelets. Some effort was required for selecting a suitable specimen, and a platelet $0.4\times0.4\times0.2$ mm was used. Weissenberg photographs showed the crystal to be monoclinic and the systematically absent reflections, hkl for $h+k=2n+1$ and $h0l$ for $l=2n+1$, indicated the space group to be Cc or C2/c. The space group was assumed to C2/c on the evidence of a centric distribution of the three-dimensional intensities.[2] The unit cell dimensions were measured on a Hilger and Watts linear diffractometer using Mo$K\alpha$ radiation ($\lambda=0.7107$ Å). Intensity data were collected with a linear diffractometer using monochromatic Mo$K\alpha$ radiation. The crystal was oriented about the b-axis, ten layers being recorded. There were 2170 independent reflections, of which 550 with $\sin\theta/\lambda\geq0.59$ Å^{-1} were too weak to be observed and were neglected for the structure determination. The intensity data were corrected for Lorentz and polarization factors and placed on an approximately absolute scale by Wilson's method. The crystal data are as follows.

Tris(π-cyclopentadienylnickel)tertiary-butylammonium; t-$C_4H_9N(\pi$-$C_5H_5Ni)_3$; MW=442.1.

Monoclinic: Space group C_{2h}^6—C2/c; $a=28.40\pm0.03$ Å, $b=9.16\pm0.02$ Å, $c=15.28\pm0.02$ Å, $\beta=100°30'\pm10'$; $Z=8$. $D_x=1.48$ g·cm^{-3}, $D_m=1.5$ g·cm^{-3} (flotation method).

The linear absorption coefficient of the substance is 28.0 cm^{-1} for Mo$K\alpha$ radiation. Thus the absorption parameter μR_{max} was 0.6, and no correction for absorption was made.

† $P(U,V,W)=\sum\sum\sum|F(hkl)|^2(1-\exp(-Q\sin^2\theta/\lambda^2))^2\cos(2\pi(hU+kV+lW))$ with $Q=30$.[3]

Determination of the Structure

Appoximate positional parameters of the three Ni atoms were determined from a modified three-dimensional Patternson function.† From a Fourier synthesis calculated with all terms phased by the Ni atoms, twelve out of the twenty non-hydrogen light atoms of the whole molecule were located. Ten of these twelve atoms were easily assigned to the carbon atoms of two cyclopentadienyl rings, and the remaining two were inferred to two carbon atoms of the t-butyl group. Further Fourier syntheses did not reveal the remaining light atoms. The coordinates of eight atoms were assumed with the use of conventional bond distances and angles. By repeating diagonal least-squares refinement with isotropic temperature factors and Fourier syntheses, all the positions of non-hydrogen atoms were obtained. Several cycles of block-diagonal least-squares refinement, minimizing the function $\sum w(k|F_o|-|F_c|)^2$, were carried out with anisotropic temperature factors for the nickel atoms and isotropic ones for all the remaining non-hydrogen atoms. A weighting scheme, $w=1$ if $F_o\geq14.0$, otherwise $w=0.2$, was used. The R index for 1620 reflections ceased to decrease at 13.8%. The final positional and temperature parameters are shown in Tables 1 and 2. The atomic numbering system is shown in Fig. 1. The temperature factors of the carbon atoms of the cyclopentadienyl groups and of the end-members of the t-butyl group are considerably large, especially for C(2), C(3), C(4), C(15), C(16), C(17), C(18) and C(19). The atomic scattering factors were taken from the International Tables for X-ray Crystallography,[5] the contribution of hydrogen atoms being disregarded. Anomalous dispersion corrections of the scattering factors were not made.

The initial solution of the structure and preliminary refinement were made with the program written by one of us (N.K.). The final refinement was performed with the program HBLS-IV[4] written by Dr. T. Ashida for HITAC-5020E computer. The table of the observed and calculated structure factors is preserved by The Chemical Society of Japan. (Document No. 7402).

TABLE 1. THE FINAL FRACTIONAL ATOMIC COORDINATES, ISOTROPIC TEMPERATURE FACTORS AND THEIR STANDARD DEVIATIONS

	x/a	y/b	z/c	B(Å^3)	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	σB(Å^2)
Ni(1)	−0.1672	0.2152	−0.1071	*	0.003 Å	0.004 Å	0.003 Å	*
Ni(2)	−0.1383	0.4479	−0.0513	*	0.004	0.004	0.003	*
Ni(3)	−0.1121	0.2295	0.0262	*	0.005	0.005	0.004	*
N	−0.1021	0.2921	−0.0929	5.7	0.030	0.033	0.030	0.7
C(1)	−0.0650	0.2850	−0.1170	2.0	0.012	0.013	0.012	0.2
C(2)	−0.0238	0.3504	−0.0965	11.0	0.045	0.049	0.045	1.3
C(3)	−0.0512	0.1278	−0.1452	14.0	0.052	0.056	0.053	1.5
C(4)	−0.0724	0.3413	−0.2101	10.0	0.041	0.045	0.041	1.1
C(5)	−0.2110	0.0241	−0.1097	8.2	0.035	0.038	0.035	0.9
C(6)	−0.2403	0.1402	−0.1099	7.3	0.032	0.035	0.032	0.8
C(7)	−0.2290	0.2202	−0.1874	10.3	0.041	0.044	0.041	1.1
C(8)	−0.2095	0.1440	−0.2659	7.5	0.033	0.036	0.033	0.8
C(9)	−0.1893	0.0283	−0.1853	8.3	0.035	0.038	0.035	0.9
C(10)	−0.1978	0.5920	−0.0551	8.2	0.035	0.038	0.035	0.9
C(11)	−0.1680	0.6057	0.0271	8.5	0.036	0.038	0.036	0.9
C(12)	−0.1188	0.6517	0.0108	7.8	0.034	0.036	0.034	0.8
C(13)	−0.1222	0.6680	−0.0810	10.0	0.041	0.044	0.041	1.1
C(14)	−0.1689	0.6469	−0.1161	8.9	0.037	0.040	0.037	1.0
C(15)	−0.0894	0.0243	0.0888	12.1	0.048	0.053	0.048	1.4
C(16)	−0.1326	0.0805	0.1225	13.0	0.050	0.055	0.051	1.5
C(17)	−0.1210	0.2215	0.1531	12.0	0.047	0.052	0.048	1.4
C(18)	−0.0653	0.2601	0.1549	11.3	0.046	0.050	0.047	1.3
C(19)	−0.0522	0.1214	0.1198	12.2	0.061	0.066	0.061	2.0

* See Table 2.

TABLE 2. TEMPERATURE FACTORS OF THE NICKEL ATOMS

The temperature factors are expressed in the form of $\exp\{-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{23}kl+B_{13}hl)\}$ with standard deviations in parentheses.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{13}
Ni(1)	0.0015(0)	0.0172(5)	0.0040(2)	−0.0002(0)	−0.0018(2)	0.0008(4)
Ni(2)	0.0015(2)	0.0159(3)	0.0039(1)	0.0001(0)	0.0007(2)	0.0005(1)
Ni(3)	0.0025(0)	0.0253(7)	0.0063(1)	0.0014(3)	−0.0013(1)	0.0018(3)

Description of the Structure and Discussion

The molecular structure is shown in Fig. 1. The three nickel atoms almost form an equilateral triangle. The *t*-butylamine group is situated perpendicularly to this triangle and the three cyclopentadienyl groups are disposed symmetrically. The molecule thus takes approximately a trigonal pyramidal structure with a symmetry C_{3v}–3m. The suggested structure for this molecule by IR, UV, and EPR studies[1] has now been confirmed.

The bond distances and bond angles associated with the nickel atoms are given in Table 3. Not much can be said about the C–C and C–N bond distances and the corresponding bond angles, since the temperature factors of the carbon atoms are large. The cyclopentadienyl groups are essentially planar, the mean deviations of atoms from the least-squares planes of these rings being 0.07, 0.04 and 0.05 Å. The average distance of the C–C bonds in the rings is 1.46 Å, though the maximum deviation amounts to 0.15 Å. The three cyclopentadienyl planes are inclined to the Ni_3 plane by amounts 68°—69° as measured from the opposite direction of the *t*-butyl group. The distances between nickel atoms and centroid of cyclopentadienyl rings are 1.81, 1.80 and 1.74 Å. The

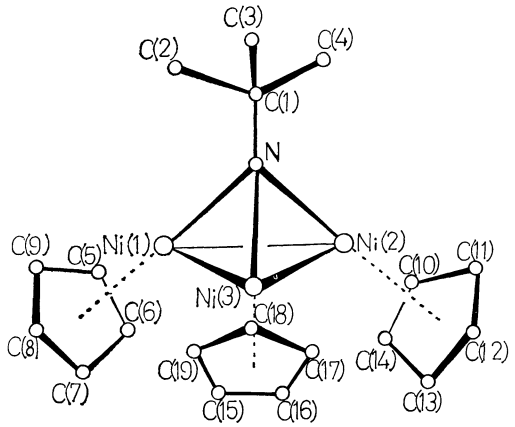

Fig. 1. Schematic representation of the molecule and the atomic numbering system.

TABLE 3. BOND DISTANCES AND BOND ANGLES (IN Å AND DEGREES)
Figures in parentheses are the standard deviations.

Ni(1)—Ni(2)	2.386(5)	Ni(2)—C(10)	2.14(4)	Ni(1)—Ni(2)—Ni(3)	59.1(4)
Ni(2)—Ni(3)	2.374(7)	Ni(2)—C(11)	2.15(4)	Ni(2)—Ni(3)—Ni(1)	60.9(4)
Ni(3)—Ni(1)	2.334(7)	Ni(2)—C(12)	2.12(4)	Ni(3)—Ni(1)—Ni(2)	60.0(4)
average	2.364	Ni(2)—C(13)	2.13(3)	average	60.0
		Ni(2)—C(14)	2.18(3)		
Ni(1)—N	1.95(2)	average	2.14	Ni(1)—N—Ni(2)	75.7(8)
Ni(2)—N	1.93(2)			Ni(2)—N—Ni(3)	74.8(9)
Ni(3)—N	1.98(3)	Ni(3)—C(15)	2.16(5)	Ni(3)—N—Ni(1)	72.9(9)
average	1.96	Ni(3)—C(16)	2.16(4)	average	74.5
		Ni(3)—C(17)	2.00(4)		
Ni(1)—C(5)	2.14(4)	Ni(3)—C(18)	2.18(4)	N—Ni(1)—Ni(2)	51.8(8)
Ni(1)—C(6)	2.18(4)	Ni(3)—C(19)	2.25(4)	N—Ni(2)—Ni(1)	52.5(9)
Ni(1)—C(7)	1.95(4)			N—Ni(2)—Ni(3)	53.4(9)
Ni(1)—C(8)	2.59(4)	average	2.15	N—Ni(3)—Ni(2)	51.8(8)
Ni(1)—C(9)	2.12(4)			N—Ni(3)—Ni(1)	53.1(9)
				N—Ni(1)—Ni(3)	54.0(9)
average	2.20			average	52.8

perpendicular distance between the apical nitrogen atom and the nickel triangle is 1.40 Å. The distance of the N–C bond is 1.18(4) Å and the mean angle N–C(1)–C is 118°(3), the numbers in parentheses being the standard deviations. The three end-carbon atoms of the t-butyl group lie almost parallel to the Ni_3 cluster plane. The Ni–N bond roughly makes a tetrahedral angle with the bonds of nickel-to-cyclopentadienyl ring. This situation is in contrast to the cases of the three congeneric complexes, $(C_5H_5Ni)_3(CO)_2$,[7] $(C_5H_5Co)_3S_2$[8] and $(C_5H_5Ni)_3S_2$,[6] where the cyclopentadienyl rings are at right angles to the metallic cluster plane. The mean value of the metal-metal distances, 2.364 Å, found in the present analysis can be compared to the value 2.39 Å, reported for $(C_5H_5Ni)_3(CO)_2$, but is considerably shorter than the values reported for $(C_5H_5Ni)_3S_2$, 2.801 Å, and for $(C_5H_5Co)_3S_2$, 2.691 Å.

A simple M.O. scheme of the metal-metal bondings based upon Cotton-Haas' calculation[9] about the $(Re_3Cl_{12})^{3-}$ ion can be used to account for the Ni–Ni distances of these compounds. Each nickel atom is bonded to the nitrogen atoms as well as to a cyclopentadienyl ring through four electron pair bonds tetrahedrally, 4s $4p^3$. The nickel-to-nickel bonding can be interpreted in terms of the interactions of the electrons. One of the five d-orbitals for each nickel atom may act as non-bonding and the remaining twelve orbitals of the three nickel atoms may form six bonding and six anti-bonding orbitals. There are 49 electrons available for the formation of the molecule; 30 from the three nickel atoms, 15 from the three cyclopentadienyl groups and 4 from the nitrogen atom. Twenty-four of these are used for the bondings for Ni-N's and Ni-cyclopentadienyl groups. Six of these enter the non-bonding orbitals. Thus the remaining 19 electrons interact between the Ni–Ni bondings. Twelve of these will occupy the bonding orbitals and seven the anti-bonding levels giving the molecule the paramagnetic character. The electronic configuration of the nickel-nickel interaction in this complex is, therefore, close to that of $(C_5H_5Ni)_3(CO)_2$ which also has 19 electrons in the nickel-nickel orbitals. With this crude scheme one may understand the close resemblance of the intermetallic distances of these two complexes. The congeneric complexes, $(C_5H_5Ni)_3S_2$ and $(C_5H_5Co)_3S_2$, have much longer intermetallic distances, having four more electrons and one more electron respectively, in the anti-bonding orbitals. The Ni–N interatomic distances as observed in the present compound, 1.93, 1.95 and 1.98 Å, are considerably longer than the sum of the covalent radii of N and Ni atoms, 1.85 Å. In $(CH_3N)_2Fe_3(CO)_9$[10] and $((C_6H_5)_2CNN)_2Fe_3(CO)_9$[11] also, the metal-nitrogen distances 1.93 and 1.95 Å are greater than the sum of the covalent radii, 1.87 Å. The mean distances between a nickel atom and the five carbon atoms of a cyclopentadienyl group are 2.20, 2.14 and 2.15 Å, which can be compared with the value 2.20 Å, reported for nickelocene.[12]

The molecular arrangement in the crystal, projected along the b-axis, is shown in Fig. 2. There are no special short intermolecular contacts in the crystal.

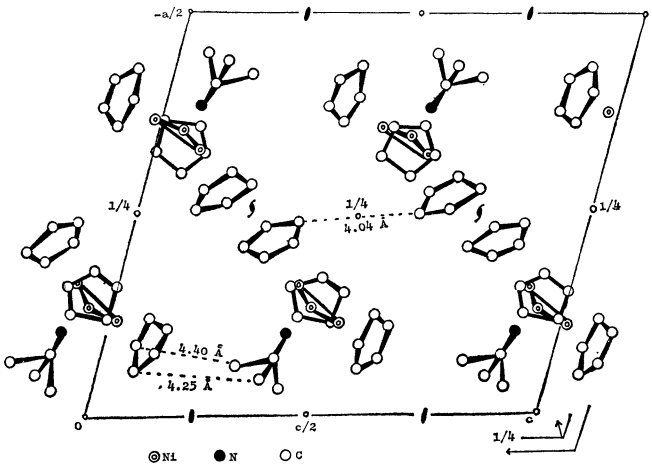

Fig. 2. Projection of the crystal structure along the b-axis (b-axis upwards).

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