Calc. for $C_{10}H_7N_3OS_2$:		C 48.20, H 2.83, N 16.86, S 25.69.
Ig	Found:	C 31.78, H 2.71, N 22.56, S 34.48.
Calc. for $C_5H_5N_3OS_2$:		C 32.09, H 2.69, N 22.46, S 34.20.
Ih	Found:	C 32.15, H 2.75, N 22.79, S 34.03.
Calc. for $C_5H_5N_3OS_2$:		C 32.09, H 2.69, N 22.46, S 34.20.

Triphenylacetyl isothiocyanate. A solution of triphenylacetyl chloride (0.01 mol) and potassium thiocyanate (0.01 mol) in acetone (30 ml) was stirred for 24 h at room temperature. Evaporation and extraction with benzene (25 ml) followed by evaporation of the resulting solution left 2.60 g (79 %) of solid material. Recrystallization from hexane and from ether gave the pure product, m.p. 115.5–116°C. (Found: C 76.55; H 4.73; N 4.08; S 9.75. Calc. for $C_{21}H_{15}NOS$: C 76.78; H 4.59; N 4.25; S 9.71).

Decomposition of 5-acylthio-1,2,3,4-thiatriazoles. Solutions in chloroform or carbon tetrachloride (about 10 %) were left at room temperature. The decomposition was followed by means of IR spectroscopy. The stability of the thiatriazoles is very much dependent on the nature of R. In some cases the decomposition was rather extensive in the compound as isolated (*e.g.* Ie), whereas in one case (Ia) the thiatriazole could be stored at room temperature for 5 days with only a little decomposition.

Acknowledgements. The author is greatly indebted to Prof. M. Ettlinger for his kind interest in this work and for inspiring discussions.

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Received February 23, 1971.

The Crystal Structure of Dodecaammine-hexa-μ-hydroxo-tetracobalt(III) Chloride

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The polynuclear cobalt(III) complex cation $(Co_4(OH)_6(NH_3)_{12})^{6+}$ studied in this work was originally synthesized by Jørgensen.[1] It belongs to the group called "Werner's brown salts" the name of which derives from the ethylenediamine analogue, synthesized by Werner in 1907.[2] He showed by cleavage experiments that in the complex three out of the four Co atoms were each bonded to four NH_3 molecules, that the fourth Co atom was not connected to ammonia, and that the complex ion had no free hydroxo groups. He suggested that the structure for the complex ion should consist of four coplanar Co atoms with trigonal symmetry in which the central Co atom had six hydroxo ligands. The central cobalt atom should form double hydroxo bridges to the three other cobalt octahedrons by sharing edges. The complex would have no symmetry centre. This was confirmed in 1914,[3] when Werner himself succeeded in resolving the complex into optically active forms, the first inorganic compound shown to be optically active. Further support, as given by Ballhausen and Jørgensen,[7] is that the absorption spectrum of the complex agrees with that derived from the mononuclear links of the suggested structure.

Jørgensen in 1892 [4] synthesized salts of a chromium(III) complex with an analogous composition, and it was suggested by Pfeiffer [5] that the structure of the two complexes were the same. A simple comparison by Schäffer [6] of the visible spectra showed, fifty years later, that this could not be the case and later bridge cleaving experiments with the Cr compound gave *cis*-diammine and *cis*-tetraammine complexes. The structure of the complex was determined by Bang and Narasimhayya.[8,9] It consists of four chromium atoms lying in a plane forming an elongated eight-membered ring alternating with four OH

groups. Two other hydroxo groups form a double bridge over the ring between the two nearest neighbour chromium atoms.[8,9]

We have now confirmed that the Co complex has the structure proposed by Werner. The compound studied was $(Co_4(OH)_6(NH_3)_{12})Cl_6,8H_2O$.

Experimental. The chloride octahydrate was prepared by precipitating a concentrated solution of the sulfate with lithium chloride.[1] When dried over conc. H_2SO_4 six H_2O were lost, which could be taken up again. Thermogravimetrical analysis showed a loss of $5\frac{1}{2}$ H_2O on heating to 80°. The same amount of water is taken up on cooling to room temperature. (Found: C 26.58; Cl 23.85; NH_3 22.92. Calc.: C 26.22; Cl 23.70; NH_3 22.73.) The crystals formed thin, flat, rather poorly developed, pale brown plates. Optical investigation indicated that they could possibly belong to the trigonal or hexagonal system. If so, the developed face was (0001).

X-Ray technique. 3-Dim. data set (Weissenberg, precession Co$K\alpha$). Crystal dimension $.34\times.25\times.03$ mm³. The crystal was rotated around the [100] axis lying in the largest extension of the crystal. The space group was $P\bar{3}$ ($P3$). a 23.90 Å; c 40.35 Å; Z 24; D_{obs} 1.87; D_{calc} 1.80. The number of reflections registered was 1195, independent reflections used in the calculations 785.

Computing methods. The least square refinements[10] were carried out on IBM 7094, other calculations on Gier. These programs were in Algol, apart from the Fourier program (Hazel and Danielsen, Dep. Inorg. Chem., B. Svejgård, Calc. Center, Aarhus University, and Lauesen and Steensgård Madsen, Inst. Datalogy, Copenhagen University).

The complex proposed by Werner contains four coplanar Co atoms and has trigonal symmetry. The space group was first taken to be $R\bar{3}$ ($R3$) from the condition for possible reflections $-h+k+l=3n$. The central Co atom had therefore to be placed on the threefold axis. This position could be seen in the 3-dim. Patterson function, which also indicated the position of the three other Co atoms.

3-Dim. Buerger min.-functions and Fourier analyses gave the positions of the nitrogen and oxygen atoms belonging to the complex and also one set of equivalent chlorine atoms. These three chlorine atoms at a distance of close packing form a layer with hydroxy and ammine groups from the complexes and are in contact with three coplanar OH groups from one side of the complex. At first glance it seemed sensible to place the other set of equivalent chlorine atoms in an analogous contact on the other side of the same complex, but this had to be excluded on account of the space group. On looking for physical evidence for a disordered structure, 32 very weak spots could be detected where the rhombohedral condition was not fulfilled. Hence it was necessary to double the a and b axes and carry out the structure determination in the space group in $P\bar{3}$ as mentioned above.

Table 1. Atomic coordinates and isotropic thermal parameters. Standard deviations .002—.006 ($R\bar{3}$).

	x	y	z	B (Å²)
Co_1	.000	.000	.236	3.2
Co_2	.198	.271	.236	4.0
O_1	.046	.153	.210	4.1
O_2	.148	.114	.262	5.2
N_1	.312	.227	.211	6.5
N_2	.244	.422	.208	6.2
N_3	.080	.311	.262	5.7
N_4	.338	.377	.267	7.0
Cl_1	.200	.298	.133	6.9
Cl_2	.333	.667	.261	6.1
O^w	.000	.000	.147	5.8
Cl,O^w	.140	.196	.331	5.0
Cl,O^w	.504	.237	.265	8.8
Cl,O^w	.385	.240	.343	9.2

Although this resulted in a sensible structural approach, it meant that the ratio between the number of observed intensities decreased so much that no reasonable refinement was possible. Refinement carried out in $R\bar{3}$ ($R=.17$) confirmed the structure suggested by Werner (Fig. 1 and Table 1). The octahedral angles are close to 90°, the Co—N 1.99—2.05 Å and Co—O 1.90—1.96 Å, which is in agreement with the results from literature. A preliminary structure investigation[11] on the corresponding ethylenediamine complex also gives four coplanar cobalt atoms but no further details.

Nitrogen and oxygen atoms form a buckled layer with the chlorine atoms in close packing on one side of the complex and an analogous layer on the other side as mentioned above. In this layer 1

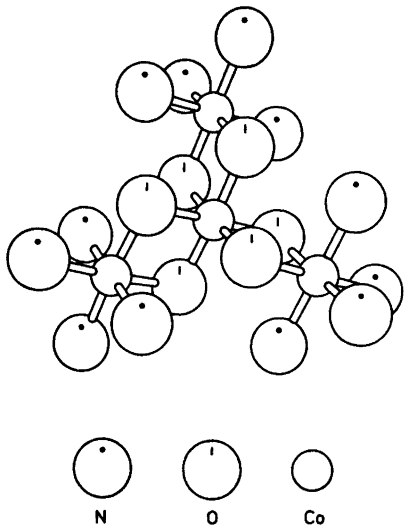

Fig. 1. The complex ion $[Co((OH)_2(NH_3)_4Co)_3]^{6+}$.

chlorine atom is on the three-fold axis and 2 water and 2 chlorine (N – Cl 3.41 – 3.45 Å) are statistically arranged. There are contacts from this layer to a statistical $Cl-H_2O$ layer around the zero plane (3.26 – 3.43 Å). The nitrogens from both sides of the complex contact the same chlorine (3.11 – 3.48 Å). The chlorine in close packing contacts a water molecule on the three-fold axis (3.21 Å).

In the direction of the three-fold axis the oxygen atoms on one side of the complex have contact to this water molecule (3.04 Å) and on the opposite side to a chlorine water layer (2.99 Å).

In the chlorine-water layer perpendicular to the three-fold axis the shortest distances of contact are $Cl-H_2O$ 3.06 Å and H_2O-H_2O 2.94 Å.

Acknowledgements. The authors are indebted to C. E. Schäffer for providing the crystals and to E. Pedersen for carrying out the thermo-gravimetric analysis.

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Received December 15, 1970.

The Temperature Dependence of the ^1H NMR Spectra of 1,1-Substituted Thiosemicarbazides. Calculation of Energy Barriers

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NMR studies of the conformation, the barriers to rotation about the N – N bonds, and the barriers to inversion at the nitrogen atoms of hydrazine derivatives have been of current interest in recent years (*cf.* Refs. 1 – 6 and references cited therein). The benzyl derivatives have been most studied owing to the simplicity of the spin system of the exchanging protons. This communication reports the energy barriers for the intramolecular exchange processes of a series of 1,1-dibenzylthiosemicarbazides (IIa-e). For comparison, the ^1H NMR spectra of 1,1-dibenzyl-4-*tert*-butylsemicarbazide (Ie), 1,1-dibenzyl-4-*tert*-butylselenosemicarbazide (IIIe), 1,1-diisopropyl-4-*tert*-butylthiosemicarbazide