with programs devised by Dr D. W. Smits. For the calculation of the bond lengths and angles, and the best plane through the ICl_4^- ion, a program devised by Dr D. Rogers was used. We wish to thank Mr H. Schurer for operating ZEBRA.

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The Crystal Structure of Decammine-μ-peroxodicobalt Pentanitrate

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(*Received* 2 *April* 1962)

The compound $[(NH_3)_5CoO_2Co(NH_3)_5](NO_3)_5$ has been prepared and its structure determined. The space group is $P4_2nm$ with $a = b = 11{\cdot}94$ and $c = 8{\cdot}06$ Å. The two cobalt atoms are linked together by a peroxide group. The bonding is similar to that in the olefin complex.

Introduction

Dinuclear cobaltic μ-peroxo coordination compounds were for the first time prepared by Fremy (1852). He prepared salts of the ion $[(NH_3)_5Co–O_2–Co(NH_3)_5]^{4+}$ and was also able to perform a complete and correct analysis of these compounds, which contain both the cobalt atoms in valency state +III and are coloured dark red. From these salts another series of salts can be prepared, which are characterized by their intense dark-green colour. The first salt in this series was prepared by Maquenne (1883). Later Vortman (1885) managed to prepare several compounds of this type. Maquenne and Vortman believed these compounds to contain an ion

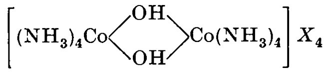
$$[(NH_3)_5Co(III).O.OH.Co(III)(NH_3)_5]^{5+} .$$

Werner & Mylius (1898) proved, however, that there were no hydrogen atoms bonded to the bridging peroxide groups. In addition to compounds with one bridge, Werner (1910) prepared dinuclear cobaltic complexes containing two or three bridges. The bridging groups could be OH^-, NH_2^- or O_2^{2-}. All these complexes were either red and diamagnetic or green and paramagnetic (Gleu & Rehm, 1938). In the red compounds the valency of the cobalt atoms is obviously +III; the cobalt valency in the green paramagnetic compounds is, however, not obvious. Both types are listed in Table 1. Werner (1910) proposed that the valency of the cobalt atoms in the green compound should be +III for one of them and +IV for the other. As the valency state +IV is very uncommon for cobalt, several authors, Gleu & Rehm (1938), Malatesta (1942), Thompson & Wilmarth (1952), Dunitz & Orgel

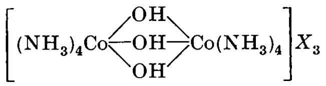
Table 1. *Some dinuclear cobalt complexes*

Red diamagnetic compounds

$[(NH_3)_5Co—O_2—Co(NH_3)_5]X_4$



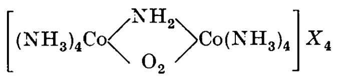
$$\left[(NH_3)_4Co\begin{matrix}OH\\ \\ OH\end{matrix}Co(NH_3)_4\right]X_4$$



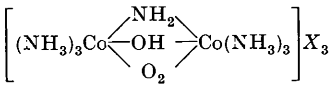
$$\left[(NH_3)_4Co\begin{matrix}OH\\ OH\\ OH\end{matrix}Co(NH_3)_4\right]X_3$$

Green paramagnetic compounds

$[(NH_3)_5Co—O_2—Co(NH_3)_5]X_5$



$$\left[(NH_3)_4Co\begin{matrix}NH_2\\ \\ O_2\end{matrix}Co(NH_3)_4\right]X_4$$



$$\left[(NH_3)_3Co\begin{matrix}NH_2\\ OH\\ O_2\end{matrix}Co(NH_3)_3\right]X_3$$

(1953), Khakham and Reĭbel (1955), Jacob & Ogorzalek (1956), proposed that the bridging group should be a superoxide group O_2^- and not a peroxide group O_2^{2-}. Then the cobalt valence would be +III for both atoms.

A paramagnetic-resonance study performed by Bernal, Ebsworth & Weil (1959) and Ebsworth & Weil (1959) showed that there are equal charges on both cobalt atoms, which could support the assumption that the atoms are linked by a superoxide link.

For all discussions mentioned so far the oxygen atoms were thought to lie on the cobalt–cobalt axis; *i.e.* the symmetry of the complex ion should be D_{4h} (Dunitz & Orgel (1953)). However, the bonding in $[(NH_3)_5Co\mu(O_2)Co(NH_3)_5]^{5+}$ is certainly of the same kind as in $[(NH_3)_4Co\mu(O_2, NH_2)Co(NH_3)_4]^{4+}$. Vlček (1960) pointed out that in the latter ion it is very difficult to place the peroxide (or superoxide) group parallel to the cobalt axis. Either there will be a very close approach of the oxygen atoms to the ammonia molecules or the distance between the cobalt atoms and the bridging amide group will be more than 3 Å, which would mean a very loose bonding, contrary to experimental results. However, if the peroxide (or superoxide) group is placed perpendicular to the cobalt axis, this obstacle is overcome.

Vlček (1960) could also show that this arrangement fits the molecular-orbital theory, with one unpaired electron distributed over the whole group $[Co–O_2–Co]^{5+}$ but mainly localized on the cobalt atoms.

Experimental

Decammine-μ-peroxodicobalt pentanitrate was prepared according to the method given by Werner & Mylius (1898).

The structure of $[(NH_3)_5CoO_2Co(NH_3)_5](NO_3)_5$

As mentioned above, single crystals of

$$[(NH_3)_5CoO_2Co(NH_3)_5](NO_3)_5$$

have a needle shape, the length being parallel to the crystallographic *c*-axis. Well developed single crystals were rotated about the needle axis and a direction perpendicular to it. All zones detectable with Fe $K\alpha$-radiation were registered using the multiple-film Weissenberg technique. Corrections for Lorentz effects and polarization but not for absorption were made.

Determination of the structure

The elementary cell was found to be tetragonal with possible space groups $P4_2/mnm$ No 136, $P4n2$ No 118 and $P4_2nm$ No 102. The last was proved to be the correct one. The elementary cell dimensions were

$$a = 11{\cdot}94 \pm 0{\cdot}02,\ c = 8{\cdot}06 \pm 0{\cdot}01\ \text{Å}\ .$$

The measured density was 1·840 g.cm^{-3} and the calculated one for two formula units in the elementary cell 1.821 g.cm^{-3}.

From a Patterson projection along the *c*-axis the positions of the cobaltic ions could be calculated. The cobalt contribution to the structure factors of reflexions of the type $h+2k=4n+2$ is small, and so less than half of the signs of reflexions of the type *hk*0 could be determined. However, from the Patterson syntheses approximate positions of the ammonia molecules could also be found. From these and the cobalt-ion positions a set of signs for the *hk*0 structure factors was calculated and a Fourier synthesis was computed. This revealed the coordination about the cobalt ions, but the positions of the nitrate groups were very obscure.

There are ten nitrate groups in the elementary cell. Packing considerations show that of these groups eight can be placed in the general positions *d* and two in the special positions *a*. Alternatively four groups can be placed in the special positions *b*, another four in *c* and two as previously in *a*. However, it is impossible to place a nitrate group in a fixed position about the position *b* without violating the symmetry restrictions. Therefore the first alternative was tried but it had to be abandoned after fruitless attempts to get agreement between the observed and calculated structure factors.

Table 2. *Parameter values for*
$[(NH_3)_5Co–O_2–Co(NH_3)_5](NO_3)_5$
Space group $P4_2nm$

Atom	Position	Number	*x*	*y*	*z*
Co	*c*	4	0·134	0·134	0·000
NH_3	*d*	8	0·213	0·054	0·181
NH_3	*d*	8	0·054	0·213	0·814
NH_3	*c*	4	0·250	0·250	0·012
O	*c*	4	0·457	0·457	0·512
N	*a*	2	0·500	0·500	0·988
N	*c*	4	0·265	0·265	0·550
N	*b*	4	0·500	0·000	0·000
O	*a*	2	0·500	0·500	0·138
O	*c*	4	0·438	0·438	0·913
O	*c*	4	0·192	0·192	0·500
O	*c*	4	0·299	0·299	0·407
O	*c*	4	0·295	0·295	0·680
O	*b*	4	rotating, $r = 1{\cdot}2$ Å		
O	*b*	4			
O	*b*	4			

It was thus indicated that all the nitrate groups occupy positions corresponding to the second alternative. The nitrate groups in *b* must then either rotate freely or else lie disordered about the given positions. With these assumptions the sign of all structure factors of type *hk*0 could be determined and reasonably accurate atomic positions could be calculated from the corresponding Fourier syntheses. The agreement between observed and calculated structure factors was much improved. The structure was refined with the aid of difference synthesis until the *R*-factor became 0·19. The structure-factor contribution of the disordered nitrate group was calculated on the assump-

Table 3. *Observed and calculated structure factors for* $[(NH_3)_5CoO_2Co(NH_3)_5](NO_3)_5$

hkl	F_o	$\|F_c\|$	α
200	—	3·1	180
400	29·0	32·5	0
600	—	2·9	0
800	8·2	2·0	0
10,0,0	—	2·3	180
12,0,0	7·9	7·9	180
110	39·0	46·2	0
210	42·7	38·1	180
310	32·9	36·3	180
410	7·3	10·2	180
510	18·5	8·9	0
610	23·5	17·2	0
710	9·7	5·7	180
810	12·8	11·2	180
910	—	2·3	0
10,1,0	5·5	2·9	180
11,1,0	7·4	9·2	180
12,1,0	3·8	3·0	0
220	68·4	68·2	0
320	20·5	14·7	180
420	—	7·1	0
520	21·4	26·4	0
620	19·4	11·4	0
720	—	7·4	0
820	—	4·7	0
920	14·6	10·6	180
10,2,0	—	6·8	0
11,2,0	—	1·5	180
330	31·5	35·4	0
430	49·5	43·7	0
530	10·3	2·7	180
630	12·9	10·6	0
730	12·5	5·6	180
830	6·6	9·8	180
930	—	0·3	180
10,3,0	10·4	10·4	180
11,3,0	8·4	3·5	0
440	54·2	51·3	0
540	7·1	6·1	0
640	10·9	8·0	180
740	6·5	7·2	0
840	14·7	8·6	180
940	—	6·2	0
10,4,0	5·6	4·5	0
550	13·4	20·3	0
650	15·8	12·7	180
750	11·7	15·3	180
850	10·3	8·5	0
950	5·4	2·5	180
10,5,0	7·1	3·8	0
11,5,0	4·3	1·5	0
660	10·4	10·1	0
760	8·3	5·0	180
860	—	4·5	0
960	9·8	8·0	0
770	16·8	22·8	0
880	9·5	18·8	0
101	63·8	60·6	12
301	50·2	50·1	186
501	3·4	7·5	186
701	10·6	10·6	312
901	6·4	5·8	347
11,0,1	11·6	16·5	188
111	11·9	12·9	119
211	15·3	20·4	181
311	43·0	43·0	185
411	12·7	22·2	187
511	6·7	12·5	22
611	—	8·0	2
711	5·5	13·4	0
811	11·5	8·6	333
911	13·1	17·6	182
10,1,1	4·0	6·4	201
11,1,1	—	5·1	4
12,1,1	3·8	4·4	348
221	42·2	42·0	173
321	8·4	4·5	157
421	9·5	8·5	161
521	—	4·1	359
621	27·2	29·3	7
721	—	4·8	16
821	8·3	7·4	186
921	—	1·0	77
10,2,1	8·6	8·8	177
11,2,1	—	4·0	13
331	—	4·6	83
431	22·6	19·8	345
531	14·4	17·7	6
631	—	3·1	34
731	—	2·8	20
831	13·1	15·4	189
931	7·4	1·3	333
10,3,1	6·0	3·6	329
11,3,1	—	2·7	202
441	8·0	24·0	16
541	13·8	13·0	358
641	15·1	15·6	178
741	31·4	25·8	187
841	4·8	11·5	8
941	6·4	5·0	181
10,4,1	—	3·0	333
11,4,1	5·3	2·4	328
551	21·0	20·3	168
651	11·3	11·6	189
751	—	2·8	172
851	—	5·0	160
951	9·5	11·3	352
661	—	6·0	164
002	99·3	95·0	3
202	13·0	10·4	319
402	19·1	15·0	138
602	6·6	9·1	169
802	16·7	20·0	21
10,0,2	5·6	5·6	173
112	17·7	16·7	351
212	23·9	30·6	191
312	13·1	18·8	173
412	24·7	24·7	332
512	7·4	13·7	159
612	25·5	20·8	350
712	16·0	12·9	23
812	6·2	4·8	223
912	—	4·9	322
10,1,2	5·5	4·0	158
11,1,2	3·5	5·8	172
222	60·1	60·6	5
322	18·0	13·7	139
422	—	2·3	339
522	29·1	30·7	3
622	—	11·8	57
722	3·4	9·0	10
822	4·4	7·6	169
922	10·6	8·7	171
10,2,2	—	2·9	82
11,2,2	—	2·6	225
332	35·0	32·6	3
432	2·2	4·5	238
532	7·2	4·3	278
632	15·5	17·2	348
732	11·9	12·4	346
832	4·0	5·3	162
932	—	7·4	170
10,3,2	3·6	3·3	359
11,3,2	3·0	1·8	54
442	35·9	34·7	11
542	6·2	5·1	253
642	7·4	6·1	186
742	—	4·1	9
842	4·9	3·1	123
942	3·2	1·7	176
10,4,2	3·2	4·1	359
552	3·8	8·8	7
652	6·0	1·0	210
752	3·5	5·6	180
103	3·1	13·1	39
303	5·5	10·4	106
503	25·3	27·4	196
703	26·9	25·3	355
903	—	2·8	319
11,0,3	4·9	3·8	208
113	17·0	16·1	201
213	22·2	22·2	123
313	—	1·8	92
413	19·8	20·8	182
513	21·6	21·0	11
613	5·3	5·9	313
713	7·9	11·0	345
813	9·1	8·7	344
913	6·6	7·1	159
10,1,3	4·0	5·8	201
223	21·6	20·0	177
323	7·8	9·3	338
423	3·5	11·7	53
523	4·2	4·6	31
623	25·6	24·1	1
723	3·3	6·5	221
823	3·7	3·2	164
923	5·5	6·4	196
10,2,3	5·8	4·1	188
333	24·6	23·4	162
433	21·0	19·9	359
533	9·0	14·0	24
633	3·2	2·4	0
733	—	3·0	53
833	11·2	15·1	195
933	6·6	4·3	207
10,3,3	—	3·5	31
443	10·4	8·5	170
543	4·8	1·5	309
643	—	4·0	74
743	10·3	4·8	190
843	4·2	3·0	190
943	2·8	1·0	217
10,4,3	4·8	3·8	346
553	4·5	6·2	132
653	6·6	3·0	211
753	4·5	1·0	35
853	—	3·1	61
953	7·1	3·6	2
10,5,3	—	1·4	66
663	7·2	1·0	277
763	—	4·0	44
863	4·9	3·3	19
773	3·5	0·7	32
873	2·4	0·5	244
883	2·0	1·5	4
004	40·3	44·3	344
204	4·5	4·5	197
404	25·6	13·6	175

Table 3 (*cont.*)

hkl	F_o	$\lvert F_c \rvert$	α
114	5·5	12·2	329
214	26·9	27·8	194
314	13·0	15·6	179
414	19·2	15·2	22
224	14·5	14·8	341
324	10·5	10·5	177
424	—	3·9	118
524	16·3	19·0	355
624	4·3	7·9	46
334	17·3	17·3	336
434	7·1	7·1	248
534	10·0	6·8	49
634	11·9	13·3	5
734	12·8	13·6	204
444	20·3	25·6	5
544	4·7	4·5	216
644	9·4	7·9	219
744	—	3·0	28
554	—	6·8	274
654	11·0	7·4	181
754	—	8·0	167
664	—	0·5	34
764	5·0	5·4	213
105	24·0	31·1	11
305	7·9	7·3	89
115	17·6	16·7	1
215	4·3	7·6	105
315	9·6	8·4	170
415	8·5	5·9	156
515	6·0	4·0	47
225	20·6	18·6	178
325	—	6·3	148
425	4·3	7·1	27
525	5·4	7·8	21
335	—	5·7	22
435	14·5	14·7	12
535	10·4	17·0	2
635	—	3·0	126
735	3·7	4·5	31
445	9·0	16·0	359
545	—	6·2	21
745	15·2	11·8	175
555	9·3	9·8	160
655	6·2	5·2	186
755	3·8	0·6	54
655	13·1	9·3	177
006	44·8	44·8	10
206	5·5	9·6	254
406	—	3·8	110
116	12·6	11·5	357
216	18·3	21·3	171
316	8·3	12·0	188
416	—	3·7	309
516	3·1	2·2	320
226	6·3	8·2	55
326	9·0	8·7	185
426	—	8·8	310
526	8·5	7·7	14
336	12·6	8·8	6
436	6·7	6·3	31
536	6·5	6·0	316
636	3·7	5·9	348
736	7·6	5·6	181
446	14·0	19·4	6
546	—	2·0	190
646	5·3	4·1	253
556	—	2·5	28
656	10·7	9·9	166
107	10·3	7·1	22
307	10·0	5·4	218
117	5·2	9·6	142
217	—	3·0	344
317	8·2	4·0	278
417	5·8	7·6	165
227	8·8	7·9	172
327	—	3·8	110
427	—	3·7	321
527	—	3·4	317
337	—	4·0	160
437	6·2	5·3	355
537	5·5	6·3	354
008	19·2	12·0	62
208	4·1	5·2	337
118	5·9	4·4	52
218	5·2	5·8	202

tion that the group rotates freely. From the projection only x and y parameters could be calculated and some of these were known only approximately, as the overlap was considerable. For the z-parameters and better x and y parameters a three-dimensional synthesis was carried out. The space group lacks a symmetry center. The z-parameter for the four cobalt ions could then arbitrarily be fixed to 0 and $\frac{1}{2}$. Further, the space-groups requirements and the *hk*0 projection solution give directly the distance between the two cobalt atoms, as well as between the cobalt atoms and two of the ligands. The N–O distance in a nitrate group is known to be 1·20 Å, and the packing distance between oxygen atoms was estimated to be 3 Å. With this knowledge approximate z parameters for all the atoms could be calculated. The real and complex parts of the structure factors and the phase angles were calculated, and the electron density could now be evaluated. This gave more accurate atomic parameters from which in its turn more accurate phase angles and electron densities could be calculated. The cycle was repeated twice. The final R factor for all reflexions was 0·20.

Description of the structure

Bond lengths and bond angles of the structure arrived at are tabulated in Tables 4 and 5. The errors are calculated according to Cruickshank's method. The geometry of the cation

$$[(NH_3)_5Co\text{–}O_2\text{–}Co(NH_3)_5]^{5+}$$

can be seen in Fig. 1. Clearly five ammonia molecules and the gravity center of the peroxide group form a somewhat distorted octahedron about the cobaltic ions. The ammonia configuration is very little distorted. The angle between two ammonia molecules situated above and below the plane of the peroxide group is, as could be expected, somewhat more than 90°. The angle between ammonia-cobalt bonds, both pointing up or both pointing down from the plane of the peroxide group, is then a little less than 90°. The rest of the bond angles between ammonia–cobalt bonds are little distorted. The bond distances between the cobaltic ions and the ammonia molecules are the expected ones.

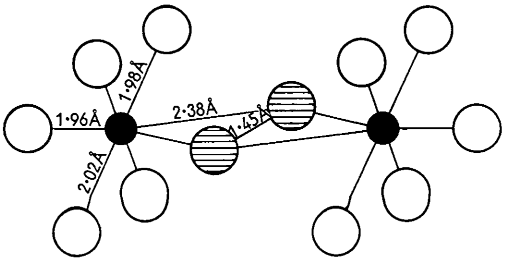


Fig. 1. The geometrical configuration of the ion $[(NH_3)_5CoO_2Co(NH_3)_5]^{5+}$.
Shaded, O; white, NH_3; black, Co.

The distances between the cobalt and the peroxide oxygens are considerably longer than usual. The geometrical configuration is the one postulated by Vlček, *i.e.* the peroxide axis is perpendicular to the connection line between the cobaltic ions. The distance between

Table 4. *Interatomic distances in* $[(NH_3)_5CoO_2Co(NH_3)_5](NO_3)_5$

Co–Co	4·52 ± 0·02 Å
Co–NH_3(I)	2·01 ± 0·04
Co–NH_3(II)	1·98 ± 0·04
Co–NH_3(III)	1·96 ± 0·04
Co–O(I)	2·38 ± 0·04
O(I)–O(I)	1·45 ± 0·06
N(I)–O(II)	1·21 ± 0·06
N(I)–O(III)	1·21 ± 0·06
N(II)–O(IV)	1·29 ± 0·08
N(II)–O(V)	1·29 ± 0·08
N(II)–O(VI)	1·17 ± 0·08
N(III)–O(VI)	1·2 ± 0·1
N(III)–O(VII)	1·2 ± 0·1
N(III)–O(VIII)	1·2 ± 0·1

Table 5. *Bond angles in* $[(NH_3)_5CoO_2Co(NH_3)_5](NO_3)_5$

NH_3(I)–Co–NH_3(I′)	86 ± 4°
NH_3(II)–Co–NH_3(II′)	84 ± 4
NH_3(I)–Co–NH_3(II′)	96 ± 4
NH_3(I)–Co–NH_3(III)	88 ± 4
NH_3(II)–Co–NH_3(III)	92 ± 4
Co–O(I)–O(I′)	72 ± 4
Co–O–Co′	144 ± 4
O(I)–Co–NH_3(I)	76 ± 4
O(I)–Co–NH_3(II)	80 ± 4

the oxygen atoms in the peroxide group is slightly but not significantly shorter than in other peroxides.

The bond lengths in the nitrate group do not deviate significantly from the values found in other nitrates. As mentioned, four of the ten nitrate ions are found to rotate. The rotation cannot be completely free as the distance between the nitrogen atoms is only 4·03 Å. Possibly the rotating nitrate ions do not form a sphere but a rotation ellipsoid. Such a rotation of nitrate groups in structures involving space-demanding cations is not uncommon.

Discussion of the structure

The structure suits the electronic description of Vlček very well. The two cobaltic ions and the bridging peroxide group are bonded together in a π-complex. The bonding *M*O-bonds are formed by the $d_{x^2-y^2}$, p_y and s orbitals of the cobalt atoms and the p_y+p_y and p_z-p_z orbitals of the peroxide group. The single electron is situated in an antibonding orbital formed by the d_{yz} orbitals of the cobalt atoms and the p_z+p_z orbital of the peroxide group. The electron is mainly localized on the cobalt atoms. The bond order of the cobalt-peroxide bond is accordingly $\frac{3}{4}$. The corresponding bond distance is also greater than that of a normal bond.

The infrared spectrum

The infrared spectrum of $[(NH_3)_5CoO_2Co(NH_3)_5](NO_3)_5$ has a strong rather broad peak at 3200 cm.$^{-1}$, a medium strong one at 1630 cm.$^{-1}$, a very strong and very broad peak about 1350 cm.$^{-1}$ and a broad double peak with maxima at 820 and 840 cm.$^{-1}$.

According to Cotton (1960) and Lawson (1961), the N–H stretching mode generally gives a strong band about 3400 cm.$^{-1}$. The formation of an ammonia–cobalt bond can be expected to shift the band towards lower frequencies. A possible hydrogen bonding should give the same result. An octahedral ammonia cobalt complex gives bands in the neighbourhood of 820 cm.$^{-1}$, 1310 cm.$^{-1}$ and 1600 cm.$^{-1}$. The first is probably due to a rocking mode, the second to a symmetric deformation and the last to an asymmetric deformation mode, all of the ammonia molecules. Nitrate ions generally give a very strong band in the neighbourhood of 1365 cm.$^{-1}$ and a strong and sharp band about 830 cm.$^{-1}$.

Accordingly the spectra can be interpreted in the following way: The first peak at 3200 cm.$^{-1}$ is due to the N–H stretching mode, the second at 1630 to a mode of the ammonia molecules in the complex ion, the peak at 1350 to overlap between bands caused by vibrations of the nitrate ion and the ammonia molecules. The peaks at 820 and 840 cm.$^{-1}$ can be attributed to a N–O mode and to a mode of ammonia.

This investigation was financially supported by the Swedish Natural Science Research Council.

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