237. *The Crystal Structure of Nitrosylpentamminecobalt Dichloride (Black Form).*

By D. Hall and A. A. Taggart.

The structure of the black form of nitrosylpentamminecobalt dichloride has been derived from a study of the three-dimensional Patterson function and the [101] projection. The crystals are orthorhombic, but, through twinning, apparent tetragonal diffraction symmetry is observed. The space-group is *Cmcm.*

The bond lengths in the complex cation appear normal except for a long *trans* cobalt–ammine bond. The bond of the nitrosyl group is collinear with the cobalt–nitrosyl bond and this cobalt–ammine bond. The interatomic separations give no suggestion of possible interactions between the complex ions.

Nitrosylpentamminecobalt dichloride can be prepared in both a black and a red form, the nature of this isomerism being as yet not explained. The red form is diamagnetic, while the black form shows variable paramagnetism, molar susceptibilities (χ_m) between $+42$ and $+3258 \times 10^{-6}$ having been reported.[1]

For the present study, samples of the black chloride were prepared, using modifications of the method of Moeller and King,[2] with χ_m varying from -29 to $+980 \times 10^{-6}$. The only apparent difference in the crystals was that those of low susceptibility were generally better formed. The densities ranged from 1·670 to 1·710 but no systematic trend could be established, although the samples of low susceptibility appeared to have slightly higher

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[1] Asmussen, Bostrup, and Jensen, *Acta Chem. Scand.*, 1958, **12**, 24.

[2] Moeller and King, *Inorg. Synth.*, 1953, **4**, 168.

densities. *X*-Ray powder photographs of samples of high and low susceptibility gave identical diffraction patterns, with no detectable change in cell dimensions. All the observed lines were in excellent agreement with the single-crystal data, and the presence of appreciable impurity was unlikely. The powder photograph of the red isomer was quite distinct.

The better-formed crystals, of low susceptibility, were used for the crystal-structure determination described in this Paper. At a late stage of the investigation, it was learned that Dr. D. Dale and Professor Dorothy Hodgkin were engaged on the same project. The two studies were completed independently and the results are essentially in agreement.[3]

EXPERIMENTAL

A sample from which the crystals were taken was analysed (Found: Cl, 28·9; Co, 24·0; N, 34·3; NH_3, 34·6. Calc. for $H_{15}Cl_2CoN_6O$: Cl, 28·9; Co, 24·1; N, 34·3; NH_3, 34·8%.

Routine powder photographs were recorded with a flat-plate camera, and selected samples photographed using a Guinier focusing powder camera. Densities were measured by flotation in a carbon tetrachloride–ethylene dibromide mixture. The crystals were black and opaque and showed a variety of faces; they were enclosed in Pyrex capillaries to prevent decomposition during photography.

Crystal Data.—$Co(NH_3)_5NOCl_2$, $M = 245{\cdot}0$, tetragonal, $a = 10{\cdot}44 \pm 0{\cdot}03$, $c = 8{\cdot}75 \pm 0{\cdot}03$ Å, $U = 953{\cdot}7$ Å,[3] $D_m = 1{\cdot}700$, $Z = 4$, $D_c = 1{\cdot}706$. Cu–K_α single-crystal Weissenberg and rotation photographs. Diffraction symmetry $4/mmm$. It was later decided that the crystals were orthorhombic with $a = b$, and that the apparent tetragonal diffraction symmetry was the result of twinning. In order to use the same convention as Dale and Hodgkin,[3] the axes have been renamed such that $a = 10{\cdot}44$, $b = 8{\cdot}75$, $c = 10{\cdot}44$ Å. The space group (deduced from the structure) is *Cmcm*. Intensity data were collected for the zero to seventh layers about [010] and for the zero layers about [100] and [101], and were estimated visually. No absorption corrections were applied. The crystals used were irregular in section, and the data cannot be of high accuracy. Several crystals were photographed, from samples of different magnetic susceptibility, but no variations in the intensity pattern were detected.

With respect to the orthorhombic axes the systematic extinctions observed were: *hkl*, absent when *h* odd, *k* even, *l* odd, or when *h* even, *k* odd, *l* even; *h*0*l*, absent when *h* odd or *l* odd. These are not specifically required by any space group, and the absences in *hkl* cannot be explained by any systematic non-space-group effect. It was assumed, then, that the crystals were twinned such that half of the domains were rotated through 90° about *b*, thus interchanging the equal-length *a*- and *c*-axes. Assuming these domains to scatter incoherently, any observed *hkl* intensity would be the sum of the *hkl* and *lkh* intensities. The observed extinctions would then be those expected for the space groups *Ccm* or *Cmcm*.

The interpretation was supported by consideration of the three-dimensional Patterson function. It proved impossible to allocate even the cobalt–cobalt vectors in a manner consistent with tetragonal symmetry, whereas, once it was assumed that the Patterson function was orthorhombic but superimposed upon a rotated image of itself, it was possible to assign all vectors involving the cobalt, chlorine, and most of the light atoms. A square-planar $Co(NH_3)_4$ group was evident, but the vector peaks involving the octahedral substituents were diffuse and not resolved. The structure appeared to be consistent with the higher space group *Cmcm*. The signs of the *hkh* structure factors were calculated on the assumption or the cobalt, chlorine, and four nitrogen atoms, and the remaining light atoms were then revealed on a [101] Fourier projection.

The projection was then refined by successive difference syntheses to a final reliability factor of 0·19. Atomic co-ordinates are listed in Table 1, and the observed structure amplitudes and calculated structure factors in Table 2. It was assumed that the nitrogen atom of the nitrosyl group was co-ordinated to the cobalt atom, but the reverse configuration could not be excluded.

Because of the superposition of *hkl* and *lkh* intensities it was not possible to refine any other projection by Fourier methods, which were the only refining techniques for which computing facilities were available. The r.m.s. structure amplitudes of the *hkl* and *lkh* terms were calculated

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[3] Dale and Hodgkin, following Paper.

for the *h*0*l* and 0*kl* zones, and the reliability factors between these and the observed structure amplitudes were 0·15 and 0·22, respectively (Table 3).

TABLE 1.

Atomic co-ordinates.

Atom	*x*/*a*	*y*/*b*	*z*/*c*	Atom	*x*/*a*	*y*/*b*	*z*/*c*
Co	9	0·280	0·250	N(3)	0	0·019	0·250
Cl	0·228	0	0	N(4)	0	0·507	0·250
N(1)	0·185	0·282	0·250	O	0	0·651	0·250
N(2)	0	0·282	0·435				

TABLE 2.

Observed structure amplitudes and calculated structure factors.

The [101] projection.

k	|*F*o|	*F*c	*k*	|*F*o|	*F*c	*k*	|*F*o|	*F*c	*k*	|*F*o|	*F*c	*k*	|*F*o|	*F*c	*k*	|*F*o|	*F*c
	0,*k*,0			1,*k*,1			2,*k*,2			4,*k*,4			5,*k*,5			6,*k*,6	
4	162	185	5	50	62	8	52	59	0	143	159	1	97	78	6	36	−20
6	57	−49	11	25	−22	10	51	−42	2	35	−24	3	69	68	8	40	32
8	61	62							4	113	94	5	63	48		7,*k*,7	
10	61	−59							6	36	−42	7	21	12	1	43	27
				2,*k*,2					8	47	47				3	35	26
			0	136	192		3,*k*,3		10	30	−38		6,*k*,6		5	34	22
	1,*k*,1		2	140	−97	1	30	−8				0	104	129		8,k,8	
1	100	107	4	98	99	3	25	13				2	39	17			
3	84	91	6	66	−66	5	31	25				4	75	81	4	27	29

TABLE 3.

Observed structure amplitudes and calculated structure factors.

Plane	|*F*o|	*F*c	r.m.s.	Plane	|*F*o|	*F*c	r.m.s.	Plane	|*F*o|	*F*c	r.m.s.	Plane	|*F*o|	*F*c	r.m.s.
								0,5,3 *	81	−70	70	0,8,6	33	28	23
(*a*) The *h*0*l* zone.								0,6,3	42	−42	42	6,8,0		−15	
0,0,2	87	71	69	2,0,10	82	−68	90	0,7,3 *	31	8	8	0,1,7 *	64	−70	70
2,0,0		−67		10,0,2		−107		0,9,3 *	62	−46	46	0,4,7	37	36	36
0,0,4	240	245	251	2,0,12	47	−45	32	0,0,4	207	254	248	0,5,7 *	95	−81	81
4,0,0		258		12,0,2		−1		4,0,0		241		0,6,7	31	−39	39
0,0,6	100	98	88	4,0,4	185	166	166	0,2,4	20	16	12	0,9,7 *	53	−58	58
6,0,0		−75		4,0,6	72	58	52	4,2,0		4		0,0,8	90	128	113
0,0,8	110	104	121	6,0,4		−47		0,4,4	132	133	128	8,0,0		98	
8,0,0		137		4,0,8	90	77	89	4,4,0		123		0,4,8	73	84	71
0,0,10	82	74	57	8,0,4		99		0,6,4	51	53	49	8,4,0		56	
10,0,0		−32		4,0,10	67	54	41	4,6,0		45		0,6,8	35	46	36
0,0,12	65	57	85	10,0,4		−22		0,8,4	55	60	57	8,6,0		22	
12,0,0		105		4,0,12	48	42	65	4,8,0		54		0,8,8	22	48	39
2,0,2	170	−193	193	12,0,4		81		0,10,4	44	48	45	8,8,0		28	
2,0,4	40	−28	24	6,0,6	140	−137	137	4,10,0		43		0,1,9 *	48	34	34
4,0,2		19		6,0,8	42	−34	29	0,1,5 *	44	14	14	0,3,9 *	75	77	77
2,0,6	153	−144	154	8,0,6		22		0,2,5	22	21	21	0,7,9 *	62	59	59
6,0,2		−163		6,0,10	70	−75	87	0,3,5 *	101	112	112	0,0,10	48	−29	52
2,0,8	40	−19	16	10,06		−97		0,4,5	62	−62	62	10,0,0		67	
8,0,2		−11		8,0,8	50	48	48	0,5,5 *	42	−29	29	0,2,10	62	85	69
								0,6,5	51	63	63	10,2,0		−48	
(*b*) The 0*kl* zone.								0,7,5 *	86	81	81	0,6,10	51	42	31
0,4,0	160	186	186	0,0,2	55	−67	69	0,8,5	46	−66	66	10,6,0		−11	
0,6,0	51	51	51	2,0,0		71		0,9,5 *	29	−20	20	0,1,11 •	37	−56	56
0,8,0	48	66	66	0,2,2	123	152	150	0,0,6	79	−73	84	0,5,11 *	44	−72	72
0,10,0	59	56	56	2,2,0		−148		6,0,0		95		0,0,12	47	92	74
0,3,1 *	83	103	103	0,6,2	79	56	55	0,2,6	108	133	123	12,0,0		50	
0,4,1	62	−74	74	2,6,0		−54		6,2,0		−112		0,2,12	33	12	22
0,5,1 *	57	−65	65	0,8,2	57	32	31	0,4,6	40	−6	18	12,2,0		−29	
0,6,1	49	69	69	2,8,0		−30		6,4,0		25		0,4,12	29	63	48
0,7,1 *	81	59	59	0,1,3 *	75	−70	70	0,6,6	66	57	49	12,4,0		25	
0,8,1	45	−70	70	0,4,3	57	41	41	6,6,0		−40					

* Apparent indices from photographs.

TABLE 4.

Bond distances and interatomic approach distances.

Bond	Length (Å)	Atoms	Distance (Å)	Atoms	Distance (Å)
Co–N(1)	1·93	Cl(3) · · · N(1)	3·62	N(3$^{\mathrm{I}}$) · · · O	3·22
Co–N(2)	1·93	Cl(3) · · · N(2)	3·49	Co($^{\mathrm{I}}$) · · · Co($^{\mathrm{II}}$)	5·66
Co–N(3)	2·28	Cl(8) · · · N(1)	3·36	Co($^{\mathrm{I}}$) · · · Cl(3)	4·30
Co–N(4)	1·99	Cl(8) · · · N(2)	3·49	Co($^{\mathrm{II}}$) · · · O	5·25
N(4)–O	1·26	Cl(3) · · · N(3)	3·54	N(4$^{\mathrm{I}}$) · · · N(4$^{\mathrm{II}}$)	5·22
		Cl(8) · · · N(4)	3·86	N(1$^{\mathrm{I}}$) · · · N(1$'^{\mathrm{III}}$)	4·58
		Cl(8) · · · O	4·08		

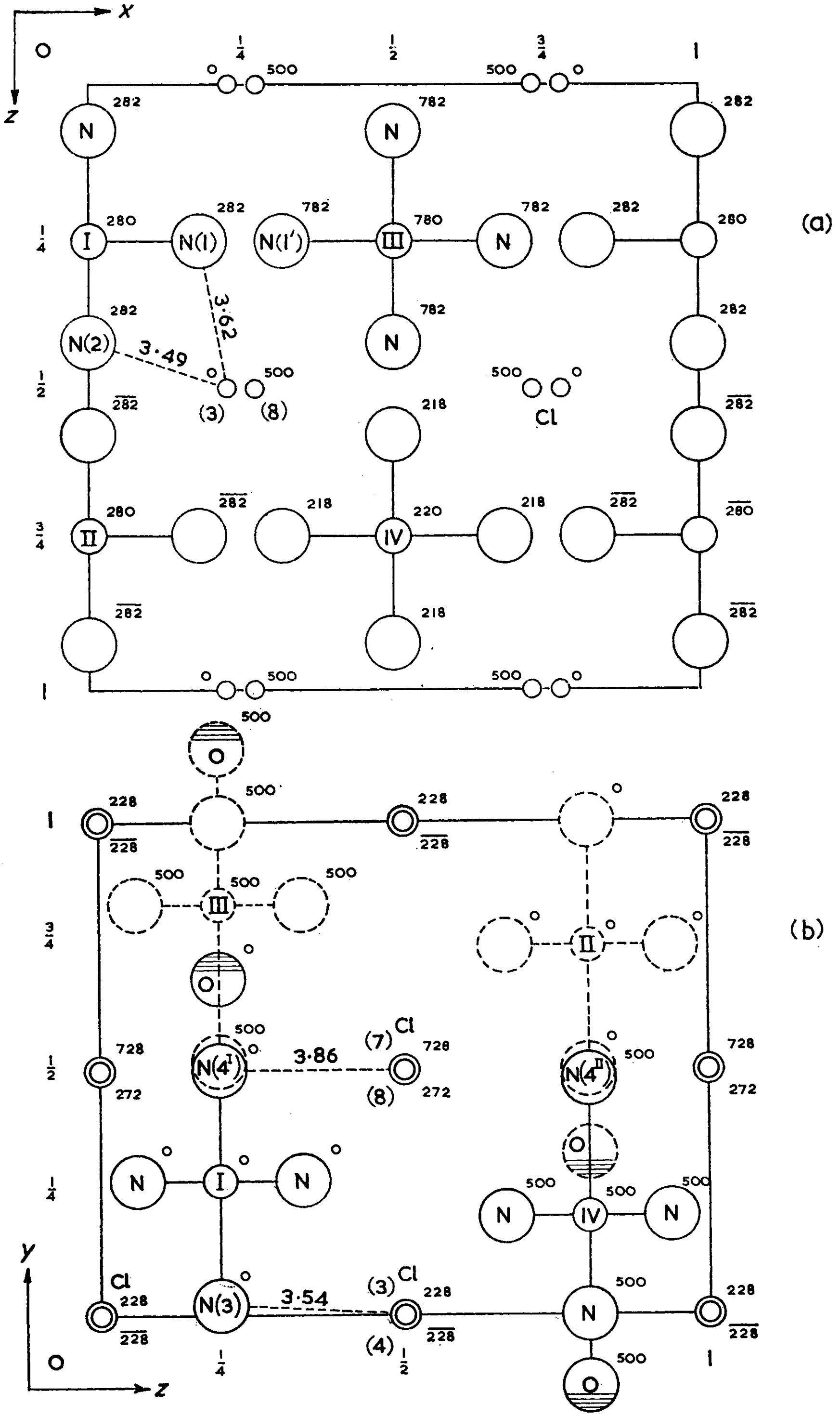

FIG. 1. Views of the structure of nitrosylpentamminecobalt(II) dichloride in projection. (a) The small numbers indicate the *y*-co-ordinates. (b) The small numbers indicate the *x*-co-ordinates. The configurations about Co(II) and Co(III) are shown as broken lines.

DISCUSSION

The structure consists of the discrete complex cations $[Co(NH_3)_5NO]^{2+}$ and chloride ions. Projected views of the structure are shown in Fig. 1, and the bond lengths in the complex cation are shown in Fig. 2. All bond angles about the cobalt atom are right angles.

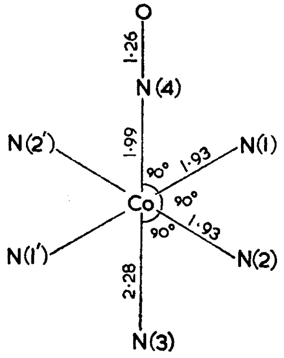

FIG. 2. Bond lengths and angles in the nitrosylpentamminecobalt(II) ion.

The bond of the nitrosyl group is collinear with the cobalt–nitrosyl bond and with the *trans* cobalt–ammine bond. The close interatomic approaches are listed in Table 4. All bond lengths in the cation except that of the *trans* cobalt–ammine bond appear to be normal.

The linear co-ordination of the nitrosyl group is surprising in that it would only be expected if the group were properly described as NO^+, where the cobalt must be present as cobalt(I). This result is not supported by chemical and spectral evidence,[4] and no unequivocal decision concerning the form of the nitrosyl group is yet possible.

All the approach distances listed in Table 4 are perfectly normal, and the structure contains no suggestion of magnetic-type interactions. The *X*-ray powder photographs do not support the existence of significant impurity or of any essential difference between the diamagnetic and paramagnetic samples of the black chloride, and no explanation of the variable paramagnetism is apparent from this work.

Calculations were performed on SILLIAC, University of Sydney, using programmes made available by Dr. H. C. Freeman.

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CHEMISTRY DEPARTMENT, UNIVERSITY OF AUCKLAND,
NEW ZEALAND.

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[4] Bertin, Mizushima, Lane, and Quagliano, *J. Amer. Chem. Soc.*, 1959, **81**, 3821.