

The Crystal Structure of a Modification of Dinitrosylcobalt Chloride, $[\text{Co}(\text{NO})_2\text{Cl}]_n$

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The crystal structure of an orthorhombic modification of dinitrosylcobalt chloride, $[\text{Co}(\text{NO})_2\text{Cl}]_n$, has been investigated by single crystal methods. The unit cell has the dimensions $a = 12.87 \text{ \AA}$, $b = 6.18 \text{ \AA}$, $c = 11.25 \text{ \AA}$, the space group being No. 55 *Pbam*. An *R* value of 0.156 has been obtained. The structure is composed of alternate layers of ordered dimeric $[\text{Co}(\text{NO})_2\text{Cl}]_2$ and disordered dimer or open $\dots\text{Cl}-\text{Co}-\text{Cl}\dots$ chains, the coordination about cobalt being approximately tetrahedral.

The existence of the dinitrosyl halides of cobalt was first reported by Hieber *et al.*^{1,2} in 1939. These compounds were formulated as $\text{Co}(\text{NO})_2\text{X}$, where $\text{X} = \text{Cl}, \text{Br}, \text{I}$, but the possibility of a dimeric structure was recognised. Subsequent investigation of the dipole moments^{3,6} in various organic solvents and of infrared absorption frequencies^{4,9} by Hieber, Beck, and Jahn seemed to confirm the concept of a dimeric molecule. In 1957, Soling and Asmussen⁵ measured the magnetic susceptibility of the dinitrosylcobalt halides and found them to be diamagnetic. Further evidence for the presence of a dimer was afforded by the preliminary crystal structure studies of Corradini *et al.*,¹⁰ a dimeric structure being indicated for the chloride, but an open chain structure for the bromide. The complex chemistry of the dinitrosylcobalt halides has been extensively investigated by Hieber and Heinicke.^{7,8} An investigation of the crystal structures of these compounds is now in progress and that of one of the modifications of the chloride has been completed.

Preparation of $[\text{Co}(\text{NO})_2\text{Cl}]_n$

Dinitrosylcobalt chloride was prepared by Soling and Asmussen's modification of the method due to Hieber *et al.*^{1,2} using an apparatus similar to that described by Soling and Asmussen.⁵ Anhydrous cobaltous chloride, prepared by the action of fuming hydrochloric acid on cobaltous carbonate, was ground together with powdered cobalt and dried at 100°C in a stream of nitrogen. Nitric oxide, purified by repeated passage through glass wool and sodium hydroxide pastilles, was then passed slowly over the mixture, the

temperature being raised gradually. The reaction commenced at *ca.* 160°C, and the passage of nitric oxide was continued for 2–3 h, after which the apparatus was evacuated to 1 mm Hg, and the product sublimed on to a “cold finger”. Black needle-shaped crystals of dinitrosylcobalt chloride were obtained, often showing extensive composite growth. It was observed during the accumulation of the X-ray data that the crystals occurred in several different orthorhombic and monoclinic modifications, indistinguishable by consideration of the external form alone.

Analysis. An analysis of the product, in which cobalt was determined electrolytically and chlorine by gravimetric determination as silver chloride, gave the following results:

	% Co	% Cl
Theoretical	38.17	22.96
Experimental (1)	38.3 ₈	23.0 ₅
Experimental (2)	38.2 ₃	23.0 ₃

CRYSTALLOGRAPHIC INVESTIGATION

Since the crystals are extremely unstable with respect to both oxygen and X-ray radiation, it would have been advantageous to have been able to mount a new crystal for each Weissenberg layer photograph. The occurrence of so many different modifications, however, made it necessary to record all data using one single crystal. A suitable crystal was mounted with its needle-axis as rotation axis, and the layers $h0l$ – $h3l$ inclusive were registered using multiple film equi-inclination Weissenberg techniques and $\text{CuK}\alpha$ radiation. Rotation photographs were also registered. The relative intensities of the 165 reflections recorded on the Weissenberg photographs were estimated visually by comparison with a standard scale.

The crystal was found to be orthorhombic with unit cell dimensions, as determined from the Weissenberg and rotation photographs: $a = 12.87 \text{ \AA}$, $b = 6.18 \text{ \AA}$, $c = 11.25 \text{ \AA}$. It was not possible to refine the cell dimensions using powder methods owing to the occurrence of different modifications in one and the same batch of crystals prepared.

Systematic absences were noted for the following reflections:

$$\begin{aligned} 0kl : k &= 2n + 1 \\ h0l : h &= 2n + 1, \end{aligned}$$

which is in accordance with space groups No. 55 *Pbam* and No. 32 *Pba2*. The centrosymmetric space group *Pbam* was employed in the initial calculations, an assumption which later proved to be correct.

The calculated density based on eight formula units of $\text{Co}(\text{NO})_2\text{Cl}$ per unit cell is 2.29 g cm^{-3} . Attempts to obtain an experimental value for the density were not successful since dinitrosylcobalt chloride is soluble in a wide range of both inorganic and organic solvents.

It appears that orthorhombic superstructures exist in which either the *a*- or the *c*-axes, or both, are doubled, the needle-axis (*b*-axis) being left unchanged. The smallest orthorhombic unit cell observed has the dimensions $a = 11.25 \text{ \AA}$, $b = 6.42 \text{ \AA}$, $c = 6.18 \text{ \AA}$, indexed in accordance with its space group, No. 63 *Cmcm*. Other crystals with the cell dimensions $a = 12.87 \text{ \AA}$, $b = 6.18 \text{ \AA}$, $c = 11.25 \text{ \AA}$ belonging to the space group *Pbam* have been studied, but their structures do not appear to be identical with that described below. Furthermore, it should be noted that Corradini *et al.*¹⁰ describe an

Table 1. Non-origin vectors ascribable to Co—Co, Cl—Cl, and Co—Cl in the “three-dimensional” Patterson synthesis, $P(uvw)$. The height of the origin peak is 3000 arbitrary units.

u	v	w	Peak height (arbitrary units)
0.0671	0.0000	0.5000	634
0.1809	0.0000	0.0000	952
0.2474	0.0000	0.5000	2201
0.4287	0.0000	0.5000	675
0.5000	0.0882	0.0000	1483
0.3183	0.1238	0.0000	486
0.0000	0.3803	0.0000	1111
0.1838	0.3803	0.0000	564
0.0688	0.5000	0.5000	845
0.2523	0.5000	0.5000	1577
0.3149	0.5000	0.0000	1144
0.4356	0.5000	0.5000	770
0.5000	0.5000	0.0000	2154

orthorhombic modification with unit cell dimensions $a = 12.81 \pm 0.10$ Å, $b = 11.11 \pm 0.10$ Å, $c = 6.14 \pm 0.05$ Å belonging to space group No. 62 $Pnma$. A monoclinic form with the cell dimensions $a = 6.36$ Å, $b = 6.18$ Å, $c = 12.63$ Å, $\beta = 120^\circ$ and space group No. 14 $P2_1/c$ (b -axis = needle-axis) is also being studied, which may perhaps be identical with the monoclinic modification reported by Corradini *et al.*¹⁰

The intensities of the reflections from the different layers were scaled together approximately assuming a linear relationship between intensity and time of exposure, and a correction was applied for Lorentz and polarisation effects. Owing to disintegration of the crystal it was not possible to record reflections about a further axis as rotation axis. A “three-dimensional” Patterson synthesis of the reflection data was performed, the non-origin vectors ascribable to Co—Co, Cl—Cl, and Co—Cl thus obtained being listed in Table 1.

It was evident that the Co and Cl atoms must eclipse one another in the direction of the needle-axis (b -axis), the vector 0.0000, 0.3803, 0.0000 indicating a Co—Cl separation of approximately 2.35 Å in that direction. If one pair of cobalt and chlorine atoms is placed in $z = 0$, *i.e.* $Pbam$, $4g$, then the other pair must occupy $Pbam$, $4h$ and thus have $z = 1/2$. It was possible to assign the following approximate positions to the Co—Cl pair in $4g$:

Co	(1)	$4g$	0.0905	0.1902	0.0000
Cl	(1)	$4g$	0.4088	0.3140	0.0000

A structure factor calculation based on these positions together with assigned temperature coefficients of 3.0 for both Co and Cl yielded a value of 0.386 for R , the reliability index.

The following approximate x - and z -parameters could be assigned to the Co—Cl pair in $4h$ by considering the interatomic vectors in Table 1:

Co	(2)	$4h$	0.3379	—	0.5000
Cl	(2)	$4h$	0.1576	—	0.5000

plausible values of the y -coordinate being:

$$y_{\text{Co}(2)} = 0.1902, \quad y_{\text{Cl}(2)} = 0.1902 \quad (\text{I})$$

$$y_{\text{Co}(2)} = 0.3140, \quad y_{\text{Cl}(2)} = 0.3140 \quad (\text{II})$$

both suggestions giving R values of 0.31 when Co(1), Co(2), Cl(1), and Cl(2) positions were included, whereas solutions of the type $y_{\text{Co}(2)} = 0.3140$, $y_{\text{Cl}(2)} = 0.1902$ led to R values > 0.40 .

A Fourier synthesis based on the signs of the structure factors obtained from the Co(1) and Cl(1) parameters alone indicated that the y -parameters for Co(2) and Cl(2) should be approximately 0.25, as did a Fourier synthesis based on the signs of the structure factors from the Co(1) and Cl(1) parameters, together with those for Co(2) and Cl(2) in which $y = 0.1902$ (I). It was realised that this might be a consequence of $K_{\text{max}} = 3$, but the possibility that $y_{\text{Co}(2)}, y_{\text{Cl}(2)} \sim 0.25$ was first investigated. The following positions were thus obtained:

Co	(1)	4g	0.0945	0.1840	0.0000
Co	(2)	4h	0.3443	0.2445	0.5000
Cl	(1)	4g	0.4130	0.3150	0.0000
Cl	(2)	4h	0.1597	0.2499	0.5000

the corresponding R value being 0.299. All possible combinations obtained by interchanging Co(1), Co(2), Cl(1), Cl(2) gave substantially higher R values, as did attempts to place them in general positions in the acentric space group $Pba2$. All the interatomic vectors listed in Table 1 could moreover be accounted for in terms of the above Co and Cl positions.

It thus seemed possible that the structure could be described in terms of a dimer situated in $z = 0$, comprising Co(1) and Cl(1), and a monomer situated in $z = 1/2$, comprising Co(2) and Cl(2). Successive Fourier difference $|F_o - F_c|$ syntheses revealed the positions of all remaining nitrogen and oxygen atoms, and a least squares refinement of the structure was performed, whereupon an R value of 0.179 was obtained, the temperature coefficient of O(2), the oxygen atom corresponding to the monomer, attaining, however, an unusually high value.

A "three-dimensional" Fourier difference synthesis after the least squares refinement indicated that there was reason to suppose that the Co(2) and Cl(2) atoms lay statistically distributed as Co(2), Co(3), Cl(2), Cl(3) in the direction of the b -axis on either side of the original Co(2), Cl(2) positions, thus comprising either an open chain-like structure similar to that described by Corradini *et al.*¹⁰ for the bromide, or a distorted dimer. Successive Fourier difference syntheses then revealed the positions of all appropriate nitrogen and oxygen atoms.

At this stage, a correction was applied for absorption, the crystal being approximated to a cylinder of cross-sectional diameter 0.08 mm. The linear absorption coefficient was calculated to be 373.4 cm^{-1} , which led to values of $\mu R = 1.60$ for the zero and first layers, $\mu R = 1.65$ for the second layer, and $\mu R = 1.70$ for the third. The layer scale factors were refined using the programme XALGLS written in Algol by Wengelin.¹¹ On further refinement of the structure, the R value converged to 0.156 and reasonable temperature coefficients were obtained for all atoms. The refinement was performed in several small steps owing to the extreme degree of disorder, and it was not possible to refine all atoms simultaneously. All temperature coefficients were refined isotropically. A "three-dimensional" Fourier difference synthesis was then calculated,

Table 2. Atomic parameters with their standard deviations and isotropic temperature coefficients. The positions indicated for Co(2), Co(3), Cl(2), Cl(3), N(2), N(3), O(2), and O(3) are only partially occupied.

Atom		x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	B
Co(1)	4g	0.09724	0.16093	0.00000	0.00080	0.00215	0.00000	4.281
Co(2)	4h	0.33986	0.18418	0.50000	0.00174	0.00530	0.00000	3.219
Co(3)	4h	0.35082	0.31543	0.50000	0.00163	0.00522	0.00000	3.297
Cl(1)	4g	0.41624	0.31823	0.00000	0.00130	0.00376	0.00000	4.102
Cl(2)	4h	0.17099	0.29786	0.50000	0.00349	0.01121	0.00000	3.082
Cl(3)	4h	0.16640	0.20936	0.50000	0.00380	0.01130	0.00000	3.098
N(1)	8i	0.15079	0.27677	0.12572	0.00190	0.00486	0.00214	0.412
N(2)	8i	0.40089	0.28545	0.36327	0.00926	0.02491	0.00983	6.035
N(3)	8i	0.43388	0.24859	0.37085	0.00500	0.01057	0.00656	1.214
O(1)	8i	0.20116	0.36318	0.19159	0.00259	0.00685	0.00316	5.137
O(2)	8i	0.43840	0.41463	0.30195	0.00386	0.00970	0.00556	1.835
O(3)	8i	0.45945	0.14703	0.29140	0.00592	0.01590	0.00767	7.430

no spurious peaks being detected. The final parameters of the atoms together with their standard deviations and isotropic temperature coefficients are given in Table 2. Observed and calculated structure factors are compared in Table 3, and an electron density projection of the structure along [010] is shown in Fig. 1.

The Lorentz-polarisation correction, the Patterson synthesis, all structure factor calculations, Fourier syntheses, and the least squares refinement were performed on the SAAB D21 computer at the University Computing Centre, Gothenburg, using programmes written by Abrahamsson *et al.*¹³⁻¹⁶ Bond distances and angles were calculated on the computer CD 3600 at the University Computing Centre, Uppsala, using the programme DISTAN written by Zalkin and modified by Lundgren and Liminga.¹⁷ Selected interatomic distances and angles are given in Table 4.

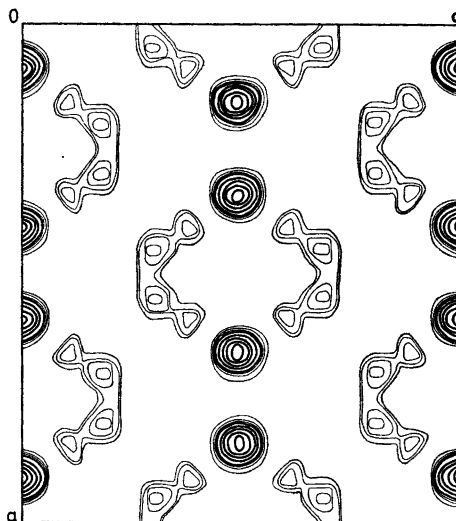


Fig. 1. Electron density projection of dinitrosylcobalt chloride along [010]. Heavy and fine lines represent contours of $10 \text{ e}/\text{\AA}^2$ and $1 \text{ e}/\text{\AA}^2$, respectively.

Table 3. Observed and calculated structure factors. All values have been multiplied by a factor of 10^3 .

<i>h k l</i>	$ F _{\text{obs}}$	F_{calc}	<i>h k l</i>	$ F _{\text{obs}}$	F_{calc}	<i>h k l</i>	$ F _{\text{obs}}$	F_{calc}
4 0 0	16235	-19793	5 1 3	2418	-2993	7 2 5	2789	2762
8 0 0	4544	-4995	6 1 3	5879	6312	10 2 5	3050	-3916
12 0 0	5500	5179	7 1 3	3419	-3632	0 2 6	11162	-9804
2 0 1	8318	7530	1 1 4	4794	4687	3 2 6	1340	-1752
6 0 1	17759	-14568	4 1 4	4611	-4633	4 2 6	4429	5248
10 0 1	9452	7454	5 1 4	4613	-4586	2 2 7	2964	-2074
0 0 2	17304	22620	7 1 4	2514	-1198	6 2 7	2759	3550
4 0 2	16729	-17902	8 1 4	5192	5919	0 2 8	9317	-9674
8 0 2	1487	787	1 1 5	3190	2951	4 2 8	3414	5227
12 0 2	5451	5540	2 1 5	4602	-4077	6 2 9	1352	2931
2 0 3	16170	19771	5 1 5	4002	-3738	0 2 10	3053	-4026
6 0 3	19784	-20899	1 1 6	3214	3593	4 2 10	1342	2329
10 0 3	8755	6895	5 1 6	3870	-4101	1 3 0	3511	-5734
0 0 4	17395	19707	8 1 6	3094	2440	5 3 0	10284	9959
4 0 4	11489	-9219	1 1 7	3178	2982	6 3 0	1373	-185
12 0 4	3344	3564	2 1 7	5569	-5200	7 3 0	2762	2525
2 0 5	5837	4965	6 1 7	3465	4280	8 3 0	2786	3216
6 0 5	16745	-13800	1 1 8	2219	1800	9 3 0	2480	-2999
10 0 5	7468	8450	1 1 9	2035	1685	11 3 0	1568	-2082
0 0 6	20590	20722	2 1 9	3954	-3627	1 3 1	5672	-6602
4 0 6	10640	-9768	1 2 0	2990	3588	2 3 1	857	773
8 0 6	1638	-1975	3 2 0	4359	-3429	5 3 1	7307	5823
2 0 7	7730	6589	4 2 0	13661	11590	6 3 1	2375	-1654
6 0 7	9864	-8384	7 2 0	2745	2885	7 3 1	4522	3854
10 0 7	2796	2999	12 2 0	3099	-3694	11 3 1	3405	-3494
0 0 8	14119	13091	2 2 1	6425	-4536	1 3 2	7958	-8623
4 0 8	9609	-9224	3 2 1	4144	-4709	3 3 2	2422	1676
2 0 9	3267	3114	6 2 1	9240	7238	4 3 2	3775	-3427
6 0 9	5100	-5648	7 2 1	3416	4032	5 3 2	7367	5893
0 0 10	9944	9305	10 2 1	2856	-3060	7 3 2	3851	3112
4 0 10	3524	-4137	11 2 1	1461	-1438	9 3 2	2718	-2387
2 1 0	1217	-619	0 2 2	12259	-15113	11 3 2	1485	-1468
3 1 0	2279	1939	1 2 2	4530	-5159	1 3 3	6714	-7443
4 1 0	10509	9145	3 2 2	1102	-1577	2 3 3	2015	-2386
5 1 0	8343	-9204	4 2 2	9951	7994	3 3 3	4097	4100
8 1 0	2263	2456	7 2 2	1510	1523	5 3 3	4996	4142
12 1 0	1896	-2817	8 2 2	1638	1448	7 3 3	4290	3399
1 1 1	4372	4949	9 2 2	1536	2309	9 3 3	1563	-1115
2 1 1	9060	-12631	12 2 2	2314	-3010	1 3 4	5723	-6074
5 1 1	4601	-4781	1 2 3	4979	-5096	5 3 4	6248	6049
6 1 1	5998	5034	2 2 3	9219	-7536	7 3 4	1543	1135
7 1 1	1964	-1919	3 2 3	1110	-910	9 3 4	1577	-1487
10 1 1	1913	-1138	6 2 3	10715	10751	1 3 5	5479	-5865
11 1 1	2087	2232	7 2 3	1897	1793	2 3 5	4061	-4234
1 1 2	6377	6207	10 2 3	4072	-4850	5 3 5	5178	4903
3 1 2	2780	-2447	11 2 3	1546	-2043	7 3 5	1459	1616
4 1 2	5175	-5733	0 2 4	13428	-7172	1 3 6	4316	-4521
5 1 2	3256	-3120	1 2 4	2051	-2679	5 3 6	4916	5361
7 1 2	1764	-1814	3 2 4	2310	-3019	7 3 6	1338	1397
8 1 2	2505	2933	4 2 4	3882	3863	1 3 7	3525	-3109
9 1 2	1822	2385	7 2 4	2279	1552	5 3 7	1932	2491
12 1 2	2594	-2667	8 2 4	1675	799	7 3 7	1715	2726
1 1 3	6442	7335	2 2 5	5974	-5568	1 3 8	2502	-3189
2 1 3	4271	2323	3 2 5	3139	-4435	5 3 8	2333	3006
3 1 3	4322	-3381	6 2 5	8246	9043	1 3 9	1579	-2447

Table 4. Selected interatomic distances and angles with their standard deviations. Distances and angles denoted by an asterisk are common to both chain and distorted dimer.

	$d \pm \sigma(d)$ Å		$\theta \pm \sigma(\theta)$ °
Co(1)—Co(1)	3.20 ± 0.02	Cl(1)—Co(1)—Cl(1)	88 ± 1
Co(1)—Cl(1)	2.33 ± 0.02	Cl(1)—Co(1)—N(1)	112 ± 1
Co(1)—Cl(1)	2.13 ± 0.03	Cl(1)—Co(1)—N(1)	116 ± 1
Co(1)—N(1)	1.73 ± 0.03	N(1)—Co(1)—N(1)	110 ± 2
N(1)—O(1)	1.12 ± 0.05	Co(1)—Cl(1)—Co(1)	92 ± 1
Co(2)—Co(3)	3.35 ± 0.04	Co(1)—N(1)—O(1)	166 ± 3
Co(2)—Cl(2)	2.28 ± 0.05	Cl(2)—Co(2)—Cl(2)	105 ± 2
Co(2)—Cl(2)*	2.39 ± 0.08	Cl(2)—Co(2)—N(2)	108 ± 4
Co(2)—Cl(3)	2.24 ± 0.05	Cl(2)—Co(2)—N(2)*	111 ± 5
Co(2)—N(2)*	1.84 ± 0.12	N(2)—Co(2)—N(2)*	114 ± 8
Co(3)—Cl(2)	2.32 ± 0.05	Cl(2)—Co(2)—Cl(3)	91 ± 2
Co(3)—Cl(3)	2.46 ± 0.06	Cl(3)—Co(2)—N(2)	114 ± 4
Co(3)—Cl(3)*	2.45 ± 0.08	Cl(3)—Co(3)—Cl(3)	100 ± 2
Co(3)—N(3)*	1.85 ± 0.07	Cl(3)—Co(3)—N(3)	120 ± 2
N(2)—O(2)*	1.16 ± 0.15	Cl(3)—Co(3)—N(3)*	106 ± 2
N(3)—O(3)*	1.14 ± 0.11	N(3)—Co(3)—N(3)*	103 ± 4
		Cl(2)—Co(3)—Cl(3)	87 ± 2
		Cl(2)—Co(3)—N(3)	125 ± 2
		Co(2)—Cl(2)—Co(2)	111 ± 2
		Co(3)—Cl(3)—Co(3)	111 ± 2
		Co(2)—Cl(2)—Co(3)	91 ± 2
		Co(2)—Cl(3)—Co(3)	91 ± 2
		Co(2)—N(2)—O(2)*	156 ± 11
		Co(3)—N(3)—O(3)*	155 ± 7

DISCUSSION

The proposed structure is illustrated in Fig. 2 (a,b,c), and can be regarded as being composed of alternate layers of ordered dimer and statistically distributed dimer, or open ...Cl—Co—Cl... chains, in $z = 0$ (Fig. 2a) and $z = 1/2$ (Fig. 2b), respectively, the corresponding nitrosyl groups being situated above and below the relevant planes. It is interesting to note that the electron density projection along [010] shows no indication of the disorder present.

The dimer formed by Co(1), Cl(1), N(1), and O(1), and outlined with continuous lines in Figs. 2a, 2c, is fairly well-defined, with Co—Cl bond lengths of 2.33 Å and 2.13 Å. The Cl—Co—Cl bond angle is 88°, the N—Co—N bond angle 110°, and the Cl—Co—N bond angles 112° and 116°. Cobalt is thus tetrahedrally coordinated, the coordination polyhedron being appreciably distorted. Bridging is accomplished through the halogen atoms, the Co—Cl—Co bond angle being 92° and the Co—Co separation 3.20 Å. This is in agreement with conclusions drawn from a study of the infrared spectrum of dinitrosylcobalt chloride.⁹ The Co—N bond length is 1.73 Å which is somewhat shorter than the sum of the covalent radii, while the N—O bond length is 1.12 Å, in agreement with the value given in Vol. III of the *International Tables*.¹⁸ The Co—N—O bond angle is 166°.

The coordination involving the remaining atoms (see Figs. 2b, 2c), is less well-defined. It is impossible from these data alone to decide whether Co(2) and Cl(2) form an open chain (dotted lines) with Co—Cl bond distances of 2.28 Å and 2.39 Å, and Co(3) and Cl(3) a similar chain (dashed lines) with

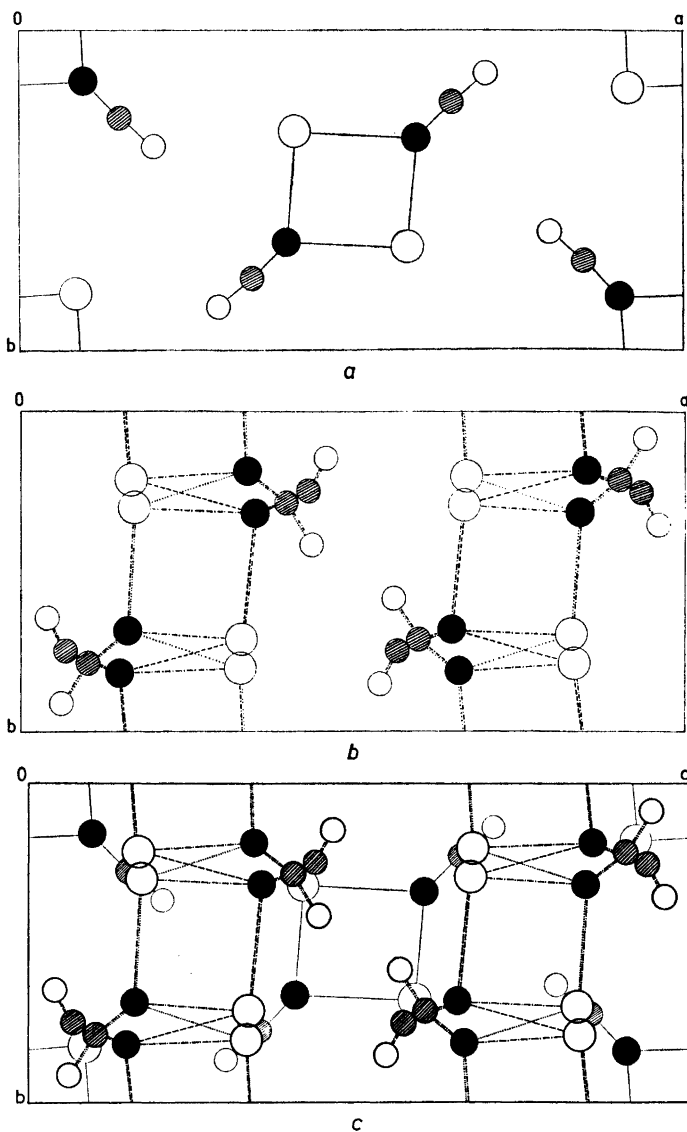


Fig. 2. A projection of the unit cell of dinitrosylcobalt chloride along [001]. Filled rings represent Co, shaded rings N, larger open rings Cl, and smaller open rings O. The possible modes of coordination of the cobalt and chlorine atoms in $z = 0$ and $z = 1/2$ are illustrated in Figs. 2a and 2b, respectively, while Fig. 2c shows the complete projection of the unit cell along [001] obtained by superimposing Fig. 2b on Fig. 2a. The nitrosyl groups are situated above and below the $z = 0$ and $z = 1/2$ planes, and for the sake of clarity, only one nitrosyl group per Co has been indicated in the figures, the other nitrosyl group being situated directly below the first at the same distance from the plane containing the corresponding Co and Cl atoms. The dotted and dashed lines in Figs. 2b and 2c delineate the two possible ...Cl—Co—Cl... chain configurations, while dash-dotted lines delineate the distorted dimer.

Co—Cl bond distances of 2.46 Å and 2.45 Å, or whether Co(3), Cl(3), Co(2), and Cl(2) form a distorted dimer (dash-dotted lines) with Co—Cl bond lengths of 2.45 Å, 2.24 Å, 2.39 Å, and 2.32 Å, respectively. In either case the coordination about cobalt is approximately tetrahedral (see Table 4 for relevant bond angles). The Co—Cl—Co bridge angles in the chains are 111°, whereas in the distorted dimer the Co—Cl—Co bridge angles are 91°, the closest distance of approach of the cobalt atoms being 3.35 Å.

On the whole, the distorted dimer seems more plausible since the structure may be derived from a monoclinic unit cell, ($P2_1/c$: $a = 6.36$ Å, $b = 6.18$ Å, $c = 12.63$ Å) containing the dimer of $Pbam$, $z = 0$, by complex twinning on the (100) plane. The disorder in $z = \frac{1}{2}$ may be reproduced if twinning of types m and c , as discussed by Ito,¹⁹ are assumed to occur simultaneously, the resulting point positions then being occupied statistically. The atoms are, however, in reality, all shifted slightly from these calculated positions. A structure factor calculation based on the positions corresponding to an ideal Ito twin gave an R value of 0.175. Evidence supporting the derivation of the structure from a monoclinic unit cell, in this way, was afforded by the absence of reflections in the $h0l$ layer not complying with the following conditions:

$$\begin{aligned} l &= 2n, \quad h = 4n \\ l &= 2n + 1, \quad h = 4n + 2 \end{aligned}$$

These extinctions could be derived from the symmetry factor of the Ito twinned lattice. Owing, however, to the alteration in the coordinates of the statistically distributed atoms as compared with those of the ideal Ito twin based on the dimer of $z = 0$, the possibility of an open chain configuration cannot be ignored. The Co—N bond lengths are 1.84 Å for Co(2)—N(2), and 1.85 Å for Co(3)—N(3), and the N—O bond lengths 1.16 Å for N(2)—O(2) and 1.14 Å for N(3)—O(3). The Co—N—O bond angles appear to deviate more from 180° than in the ordered dimer and are approximately 155° but it is difficult, owing to the paucity of the data, to say how much importance should be attached to these deviations from linearity and whether or not a spatial arrangement similar to that described by Alderman and Owston¹² is present.

Studies of the crystal structures of other orthorhombic and monoclinic modifications of dinitrosylcobalt chloride are in progress, a dimeric structure being indicated in at least one monoclinic form ($a = 6.36$ Å, $b = 6.18$ Å, $c = 12.63$ Å, $P2_1/c$). The crystal structures of the bromide and the iodide are also under consideration.

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