

also in the trigonal bipyramidal Cu<sup>II</sup> complex, [Cu(trenen)]<sup>2+</sup> (Cannas, Cristini & Marongiu, 1976). Thus, the stronger affinity of the secondary N atom of trenen for metal centres is not restricted to the peroxo dimer nor is it restricted to octahedral Co<sup>III</sup> complexes, with the exception of the azido complex, [Co(trenen)N<sub>3</sub>]<sup>2+</sup>, where Co—N(sec) is indistinguishable from four of the other Co—N distances (Maxwell, 1971); the effect appears to be independent of the ligand *trans* to the secondary N and is therefore ligand derived. The azido complex is unusual in the sense that the azido group introduces steric effects which lengthen one of the *cis*-Co—N(prim) distances. The azido group may also influence the Co—N(sec) distance. It is interesting to note in the case of [Co(tetraen)Cl]<sup>2+</sup>, where the ligand tetraen is the long chain analogue of trenen, the Co—N distance to all secondary N atoms, including that *trans* to the chloride, is indistinguishable from that to the primary N atoms (Snow, 1970). The structure of the complex, [Co(Metrenen)Cl]<sup>2+</sup>, is somewhat different (Buckingham, Dwyer, Sargeson & Watson, 1972). The chloride is now *trans* to the tertiary N which exhibits the shortest Co—N distance [1.923 (3) Å], shorter than that to the secondary N atom. Steric hindrance introduced by the methyl group may be responsible for the longer Co—N(sec) bond when compared with that found in the unmethylated complex, [Co(trenen)Cl]<sup>2+</sup>, reported here.

The rate of base-catalyzed hydrolysis of [Co(trenen)Cl]<sup>2+</sup> is much faster than for [Co(NH<sub>3</sub>)<sub>5</sub>Cl]<sup>2+</sup> (Buckingham, Marzilli & Sargeson, 1969). This has been attributed to the greater acidity of the proton on the secondary N which is *trans* to the leaving group, Cl<sup>-</sup>. Deprotonation results in the donation of electron density onto Co<sup>III</sup> which weakens the bond to the leaving group and facilitates the

formation of the five-coordinate intermediate through which substitution reactions on Co<sup>III</sup> are widely believed to occur (Buckingham, Dwyer, Sargeson & Watson, 1972; Buckingham, Marzilli & Sargeson, 1969). The structure of [Co(trenen)Cl]<sup>2+</sup> indicates that the greater acidity of the secondary amine can be attributed to its shorter Co—N distance when compared with that of the primary amine.

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## Structures of Dichlorobis(trimethylamine oxide)cobalt(II), Diiodobis(trimethylamine oxide)cobalt(II), Dichlorobis(trimethylamine oxide)zinc and Dibromobis(trimethylamine oxide)zinc

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**Abstract.** [CoCl<sub>2</sub>(C<sub>3</sub>H<sub>9</sub>NO)<sub>2</sub>] (1), *M<sub>r</sub>* = 280.1, orthorhombic, *Pna*2<sub>1</sub>, *a* = 40.800 (10), *b* = 10.882 (5), *c* = 10.966 (5) Å, *V* = 4868.7 (33) Å<sup>3</sup>, *Z* = 16, *D<sub>m</sub>* = 1.47

(room temperature), *D<sub>x</sub>* = 1.53 (150 K) g cm<sup>-3</sup>, λ(Mo Kα) = 0.71069 Å, μ = 18.26 cm<sup>-1</sup>, *F*(000) = 2320, *T* = 150 K, *R* = 0.0564 for 2605 observed

Table 1. *Crystal data and structure analyses*

	[CoCl <sub>2</sub> (Me <sub>3</sub> NO) <sub>2</sub> ] (1)	[CoI <sub>2</sub> (Me <sub>3</sub> NO) <sub>2</sub> ]* (2)	[ZnCl <sub>2</sub> (Me <sub>3</sub> NO) <sub>2</sub> ] (3)	[ZnBr <sub>2</sub> (Me <sub>3</sub> NO) <sub>2</sub> ]* (4)
Crystal size (mm)	0.29 × 0.21 × 0.23	0.28 × 0.21 × 0.23	0.43 × 0.32 × 0.25	0.19 × 0.23 × 0.21
Crystal form	Capped prism	Prism	Tabular	Tabular (bevelled)
2θ <sub>max</sub> (°)	50	50	50	60
h scan range	0–49	0–16	0–15	0–15
k scan range	0–13	0–15	0–15	0–15
l scan range	0–14	0–14	–11–11	0–14
Standard reflections	18, 0, 0, 040, 004	400, 040, 004	300, 040, 002	400, 040, 004
Reflections measured	4836	2311	2572	4060
Unique reflections	4508	2016	2457	1861
Reflections used	2605 [ <i>I</i> > 3σ( <i>I</i> )]	1424 [ <i>I</i> > 3σ( <i>I</i> )]	1704 [ <i>I</i> > 3σ( <i>I</i> )]	1322 [ <i>I</i> > 2σ( <i>I</i> )]
R <sub>int</sub> (merging)	0.0242	0.0140	0.0115	–
Transmission range	0.794–0.654	0.647–0.482	0.876–0.723	0.936–0.588
Parameters refined	268	97	136	61
Weighting, <i>g</i>	0.0002	0.0006	Unit weights	0.00014
Treatment of H atoms	Riding model†	Parameters refined‡	Riding model§	Riding model
Refinement (Δ/σ) <sub>max</sub>	0.008†	0.155‡	0.057§	0.002
Residual density (e Å <sup>-3</sup> )	0.99, –0.56	0.83, –1.10	1.06, –0.51	1.18, –0.84
S	1.65	0.98	0.96	1.19
R, wR	0.0564, 0.0605	0.0256, 0.0334	0.0359, 0.0405	0.0452, 0.0364

\* [CoBr<sub>2</sub>(Me<sub>3</sub>NO)<sub>2</sub>] is isomorphous with the [CoI<sub>2</sub>(Me<sub>3</sub>NO)<sub>2</sub>, [ZnBr<sub>2</sub>(Me<sub>3</sub>NO)<sub>2</sub>] pair, having the same *Pbcn* space group, and cell parameters: *a* = 11.234 (6), *b* = 11.047 (11), *c* = 10.185 (4) Å.

† Rotational refinement of CH<sub>3</sub> groups excluded. H atoms were not fixed to the C(1), C(2), C(3), C(10), C(11), C(12) atoms which show high temperature factors.

‡ H atoms located; positions refined, but subject to C–H = 0.96 Å.

§ Rotational refinement of CH<sub>3</sub> groups included.

reflections. The compound contains Co in four coordination, but the precise geometry varies somewhat over four molecules which are present in the asymmetric unit. The differences are reflected in significant variations in the Cl–Co–Cl and O–Co–O bond angles. [CoI<sub>2</sub>(C<sub>3</sub>H<sub>9</sub>NO)<sub>2</sub>] (2), *M<sub>r</sub>* = 462.95, orthorhombic, *Pbcn*, *a* = 11.742 (4), *b* = 11.291 (3), *c* = 10.404 (3) Å, *V* = 1379.4 (7) Å<sup>3</sup>, *Z* = 4, *D<sub>m</sub>* = 2.15 (room temperature), *D<sub>x</sub>* = 2.23 (150 K) g cm<sup>-3</sup>, μ(Mo *Kα*) = 56.53 cm<sup>-1</sup>, *F*(000) = 868, *T* = 150 K, *R* = 0.0256 for 1424 observed reflections. The compound is a mononuclear tetrahedral Co complex with molecular symmetry *C*<sub>2</sub>. [ZnCl<sub>2</sub>(C<sub>3</sub>H<sub>9</sub>NO)<sub>2</sub>] (3), *M<sub>r</sub>* = 286.5, monoclinic, *P2<sub>1</sub>*, *a* = 9.756 (3), *b* = 10.383 (3), *c* = 6.558 (2) Å, β = 109.13 (2)°, *V* = 627.6 (3) Å<sup>3</sup>, *Z* = 2, *D<sub>m</sub>* = 1.47 (room temperature), *D<sub>x</sub>* = 1.52 (150 K) g cm<sup>-3</sup>, μ(Mo *Kα*) = 24.11 cm<sup>-1</sup>, *F*(000) = 296, *T* = 150 K, *R* = 0.0359 for 1704 observed reflections. The molecular symmetry approximates to *C*<sub>2</sub>. [ZnBr<sub>2</sub>(C<sub>3</sub>H<sub>9</sub>NO)<sub>2</sub>] (4), *M<sub>r</sub>* = 375.4, orthorhombic, *Pbcn*, *a* = 11.270 (3), *b* = 11.053 (3), *c* = 10.206 (3) Å, *V* = 1271.3 (6) Å<sup>3</sup>, *Z* = 4, *D<sub>m</sub>* = 1.91 (room temperature), *D<sub>x</sub>* = 1.96 (150 K) g cm<sup>-3</sup>, μ(Mo *Kα*) = 81.85 cm<sup>-1</sup>, *F*(000) = 736, *T* = 150 K, *R* = 0.0447 for 1322 observed reflections. The compound is isomorphous with (2). The molecular packing in (2) and (4) is suited to the heavier halides, even though there are *X*⋯*X* intermolecular distances as low as *ca* 4.9 Å. With the chlorides, greater *M*–*X* bond polarity and the likelihood of shorter *X*⋯*X* distances causes development of alternative structures, as shown by (1) and (3).

**Introduction.** Reaction of Co halides with monodentate ligands commonly produces tetrahedral complexes of composition Co*X*<sub>2</sub>*L*<sub>2</sub>, although derivatives of the alternative type Co*X*<sub>2</sub>*L*<sub>3</sub> are sometimes formed (Issleib & Kreibich, 1961). The former class was the subject of extensive spectroscopic study at an early stage (as examples: Cotton, Barnes & Bannister, 1960; Drago, Donoghue & Herlocker, 1965; Hunter, Langford, Rodley & Wilkins, 1968). X-ray structure determinations have since been made on various individual compounds, *e.g.* CoCl<sub>2</sub>(Me<sub>3</sub>PO)<sub>2</sub> (Edelmann & Behrens, 1986). Arising out of one spectroscopic study on Co halide Co*X*<sub>2</sub>*L*<sub>2</sub> complexes with trimethylamine oxide (tmno) (Herlocker & Drago, 1968), it was suggested that their electronic spectra obtained from solutions and from the solids are so different as to indicate that in the crystalline condition there is ligand bridging to give five-coordination (Herlocker, 1969). But as has been remarked quite recently, there is a paucity of structural information on tmno compounds generally (Goggin, 1987). With our current interest in the structures of oxo-ligand complexes, we are addressing some remaining questions on Co halide complexes, now with tmno, and later with pyridine *N*-oxide (pyo).

We first determined the crystal structure of [CoCl<sub>2</sub>(Me<sub>3</sub>NO)<sub>2</sub>] (1). As evidenced by the intense blue colour, the molecules in the crystal contain four-coordinate Co, but somewhat unexpectedly the asymmetric unit was found to comprise four molecules showing conformational differences. However, determination of the structure of [CoI<sub>2</sub>(Me<sub>3</sub>NO)<sub>2</sub>] (2), and of the zinc compounds [ZnCl<sub>2</sub>(Me<sub>3</sub>NO)<sub>2</sub>] (3) and [ZnBr<sub>2</sub>(Me<sub>3</sub>NO)<sub>2</sub>] (4) for comparison showed

Table 2. Atom coordinates ( $\times 10^4$ ) and equivalent isotropic temperature factors ( $\text{\AA}^2 \times 10^3$ ) with e.s.d.'s in parentheses

$U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor. For (1) Co and Cl atoms only were refined anisotropically.

	x	y	z	$U_{eq}$
<b>[CoCl<sub>2</sub>(Me<sub>3</sub>NO)<sub>2</sub>] (1)</b>				
Co(1)	1298 (1)	2141 (2)	-1132	30 (1)
Co(2)	4898 (1)	7788 (2)	41 (2)	17 (1)
Co(3)	2487 (1)	7403 (20)	-899 (2)	18 (1)
Co(4)	1292 (1)	7250 (2)	4675 (2)	18 (1)
Cl(11)	1805 (1)	2956 (5)	-852 (5)	61 (2)
Cl(12)	919 (1)	3560 (4)	-516 (5)	51 (2)
Cl(21)	4685 (1)	7110 (4)	-1731 (4)	27 (1)
Cl(22)	5448 (1)	7520 (4)	-33 (4)	31 (1)
Cl(31)	2076 (1)	8632 (4)	-190 (4)	22 (1)
Cl(32)	2944 (1)	8384 (4)	-1596 (4)	27 (1)
Cl(41)	880 (1)	8620 (4)	4289 (4)	27 (1)
Cl(42)	1765 (1)	8135 (4)	4038 (4)	30 (1)
O(11)	1228 (3)	1479 (11)	-2738 (11)	38 (3)
O(12)	1220 (2)	521 (8)	-388 (10)	16 (2)
O(21)	4727 (3)	7148 (11)	1612 (10)	26 (3)
O(22)	4744 (2)	9479 (9)	59 (11)	27 (3)
O(31)	2244 (2)	6614 (9)	-2182 (9)	16 (3)
O(32)	2689 (2)	6572 (9)	466 (9)	21 (3)
O(41)	1285 (2)	6636 (9)	6353 (9)	22 (3)
O(42)	1205 (2)	5613 (9)	4077 (10)	23 (3)
N(11)	1271 (3)	2190 (11)	-3801 (11)	20 (3)
N(12)	1207 (3)	337 (11)	898 (11)	14 (3)
N(21)	4816 (3)	6032 (13)	2132 (13)	32 (4)
N(22)	4825 (3)	10346 (13)	986 (13)	30 (4)
N(31)	2401 (3)	5812 (12)	-3038 (12)	21 (3)
N(32)	2520 (3)	5813 (12)	1229 (12)	21 (4)
N(41)	1312 (3)	7427 (11)	7382 (11)	20 (3)
N(42)	1145 (3)	5326 (12)	2848 (12)	22 (3)
Cl(1)	1046 (5)	1549 (20)	-4717 (22)	74 (7)
Cl(2)	1146 (7)	3456 (28)	-3502 (28)	113 (11)
Cl(3)	1602 (5)	2028 (23)	-4111 (24)	86 (8)
Cl(4)	1247 (4)	-1032 (13)	1094 (16)	21 (4)
Cl(5)	1486 (4)	991 (15)	1528 (15)	24 (4)
Cl(6)	905 (4)	718 (15)	1372 (15)	25 (4)
Cl(7)	4562 (4)	5677 (15)	3014 (15)	30 (5)
Cl(8)	4836 (4)	5052 (14)	1184 (16)	33 (5)
Cl(9)	5147 (3)	6196 (15)	2763 (15)	21 (4)
Cl(10)	4592 (5)	11435 (24)	850 (26)	93 (9)
Cl(11)	4889 (5)	9899 (21)	2192 (21)	67 (7)
Cl(12)	5123 (7)	10803 (25)	449 (29)	112 (11)
Cl(13)	2128 (4)	4988 (16)	-3473 (18)	41 (5)
Cl(14)	2668 (4)	5048 (15)	-2450 (16)	27 (5)
Cl(15)	2530 (4)	6545 (16)	-4071 (16)	31 (5)
Cl(16)	2386 (4)	5579 (15)	2330 (14)	18 (4)
Cl(17)	2551 (4)	5194 (15)	715 (15)	24 (4)
Cl(18)	2772 (4)	4946 (16)	1788 (16)	31 (5)
Cl(19)	1574 (3)	8335 (13)	7216 (14)	13 (4)
Cl(20)	1397 (4)	6573 (14)	8436 (14)	23 (4)
Cl(21)	991 (4)	8039 (15)	7613 (16)	25 (4)
Cl(22)	842 (4)	5932 (18)	2392 (19)	45 (5)
Cl(23)	1443 (4)	5676 (15)	2153 (15)	24 (4)
Cl(24)	1115 (4)	3941 (15)	2774 (18)	39 (5)

	x	y	z	$U_{eq}$
<b>[CoI<sub>2</sub>(Me<sub>3</sub>NO)<sub>2</sub>] (2)</b>				
I	4600 (1)	2097 (1)	5397 (1)	16 (1)
Co	5000	3366 (1)	7500	12 (1)
O	6314 (3)	4187 (4)	6849 (4)	17 (1)
N	7085 (4)	4865 (4)	7601 (5)	14 (1)
Cl(1)	6458 (5)	5516 (6)	8638 (6)	21 (2)
Cl(2)	7635 (5)	5721 (6)	6693 (6)	21 (2)
Cl(3)	7958 (5)	4050 (6)	8154 (6)	21 (2)

	x	y	z	$U_{eq}$
<b>[ZnCl<sub>2</sub>(Me<sub>3</sub>NO)<sub>2</sub>] (3)</b>				
Zn	7954 (1)	5000	7091 (1)	9 (1)
Cl(1)	6272 (1)	4891 (2)	8800 (2)	20 (1)
Cl(2)	10298 (1)	5106 (3)	9207 (2)	22 (1)
O(1)	7937 (4)	3468 (4)	5299 (7)	21 (1)
N(1)	6719 (5)	2689 (5)	4358 (8)	18 (1)
Cl(11)	5369 (6)	3476 (6)	3437 (9)	22 (2)
Cl(12)	7016 (9)	1955 (8)	2559 (14)	26 (3)
Cl(13)	6549 (7)	1797 (6)	6036 (10)	26 (2)
O(2)	7195 (4)	6474 (4)	5203 (7)	20 (1)
N(2)	8081 (5)	7224 (4)	4340 (7)	17 (1)
Cl(21)	9042 (6)	6382 (6)	3536 (9)	20 (2)
Cl(22)	7066 (9)	7948 (9)	2482 (16)	28 (3)
Cl(23)	8966 (7)	8137 (7)	6040 (11)	28 (2)

Table 2 (cont.)

	x	y	z	$U_{eq}$
<b>[ZnBr<sub>2</sub>(Me<sub>3</sub>NO)<sub>2</sub>] (4)</b>				
Zn	5000	3248 (1)	7500	14 (1)
Br	4560 (1)	2132 (1)	5519 (1)	17 (1)
O	6317 (4)	4196 (4)	6822 (4)	20 (1)
N	7105 (4)	4880 (4)	7598 (5)	17 (1)
Cl(1)	6461 (5)	5500 (5)	8683 (6)	20 (2)
Cl(2)	7636 (6)	5812 (6)	6721 (6)	25 (2)
Cl(3)	8047 (6)	4064 (6)	8126 (6)	24 (2)

only a single molecular conformation in each case. This report deals with the structures of these four compounds.

**Experimental.** The compounds were prepared by reaction of equivalent proportions of the metal halide and trimethylamine oxide in ethanol containing sufficient triethoxymethane (tem) to maintain anhydrous conditions (Brodie, Hunter, Rodley & Wilkins, 1968). The Zn compounds required recrystallization from ethanol to give analytically pure products. The electronic spectra of the Co compounds (1) and (2), and of the bromide  $[\text{CoBr}_2(\text{Me}_3\text{NO})_2]$ , as obtained both from solutions in methylene chloride and from the solids, matched those reported by Herlocker & Drago (1968). Crystals of (2) suitable for diffractometry were obtained by diffusion of a top layer of ether into a solution in nitromethane. In other cases, crystals were from dilute mother liquors which had been decanted after separation of most of the primary crop. The crystals were rinsed with tem and ether, and dried under a nitrogen stream. Crystal densities measured at room temperature were obtained by flotation in chloroform (or bromoform) mixtures with petrol ether.

**X-ray analysis.** Data collected using Nicolet R3m four-circle diffractometer, graphite-monochromated Mo K $\alpha$  radiation,  $\omega$ -scan mode with crystal at 150 K; crystal stabilities monitored, but no significant variations. Space groups were initially indicated by systematic absences and confirmed by the successful structure refinements. For (1), with space group  $Pna2_1$ , it was checked that atomic coordinates could not be accommodated in the higher symmetry  $Pnma$ . Cell parameters from least-squares refinement of 25 automatically centred reflections within the range  $2\theta = 13$ – $35^\circ$ ; absorption corrections from  $\psi$  scans. Heavy atoms located from Patterson map, and remaining non-H atoms from difference Fourier syntheses. Least-squares refinement to minimize function  $\sum w(|F_o| - |F_c|)^2$ , with reflection weights  $w = [\sigma^2(F_o) + g|F_o|^2]^{-1}$ . For (1) Co and Cl atoms only were refined anisotropically. In all cases H atoms were inserted (or constrained) at the idealized C—H distance of 0.96 Å. For (1) and (3) with non-centrosymmetric space groups the absolute configuration which gave the better refinement was chosen.

Table 3. Bond lengths (Å) and angles (°) for [CoCl<sub>2</sub>(Me<sub>3</sub>NO)<sub>2</sub>] (1) with e.s.d.'s in parentheses

	Co(1)*	Co(2)*	Co(3)*	Co(4)*	Average
Co—Cl	2.272 (5), 2.286 (5)	2.253 (5), 2.263 (4)	2.284 (4), 2.281 (5)	2.286 (4), 2.265 (4)	2.274
Co—O	1.924 (12), 1.969 (9)	1.985 (11), 1.945 (10)	1.923 (10), 1.933 (10)	1.958 (10), 1.932 (10)	1.946
O—N	1.409 (17), 1.425 (16)	1.388 (18), 1.426 (18)	1.433 (16), 1.413 (16)	1.424 (15), 1.404 (17)	1.415
Cl—Co—Cl	108.1 (2)	108.0 (2)	116.2 (2)	106.9 (2)	†
O—Co—O	91.2 (5)	102.1 (5)	125.2 (4)	90.1 (4)	†
Co—O—N	122.2 (9), 122.8 (7)	124.9 (9), 123.9 (9)	121.4 (7), 124.5 (8)	122.5 (8), 124.3 (8)	123.3‡

\* Indicates the Co atom at the centre of each of the four molecules in an asymmetric unit.

† With large deviations shown by the Co(3) molecule, averages are not meaningful.

‡ Comparison of this value with that for Co—O—P in [CoCl<sub>2</sub>(Me<sub>3</sub>PO)<sub>2</sub>], 131.5° (Edelmann & Behrens, 1986), is valid. A corresponding value obtained by us for this Me<sub>3</sub>PO compound at 150 K was 129.7°.

Table 4. Bond lengths (Å) and angles (°) for (2), (3) and (4) with e.s.d.'s in parentheses

	[CoI <sub>2</sub> (Me <sub>3</sub> NO) <sub>2</sub> ]* (2)	[ZnBr <sub>2</sub> (Me <sub>3</sub> NO) <sub>2</sub> ]* (4)	[ZnCl <sub>2</sub> (Me <sub>3</sub> NO) <sub>2</sub> ] (3)	[ZnCl <sub>2</sub> (pyo) <sub>2</sub> ]†
M—X	2.658 (1)	2.420 (1)	2.273 (1), 2.255 (1)	2.214 (1)
M—O	1.923 (4)	1.944 (4)	1.975 (5), 1.956 (4)	1.992 (2)
O—N	1.421 (6)	1.409 (6)	1.402 (6), 1.412 (7)	1.338 (4)
X—M—X	114.7 (1)	118.7 (1)	116.7 (1)	119.5 (1)
O—M—O	122.4 (3)	114.8 (3)	109.0 (2)	106.8 (2)
M—O—N	125.2 (4)	124.7 (3)	124.5 (4), 122.1 (3)	120.4 (1)
Interplane‡	80.8	78.7	80.6	

\* Isomorphous pair: (2) and (4).

† Comparative data on the pyo complex from McConnell, Day & Wood (1986).

‡ Angle between metal-oxygen and metal-halogen planes.

Details on individual crystals, with results of refinements are given in Table 1.

The packages of integrated programs, *SHELXTL*, version 4.1 (Sheldrick, 1985) and *SHELXTL PC* (Sheldrick, 1990) were used for data processing, structure solution and refinement. Atomic scattering factors therein are from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Atomic coordinates are given in Table 2 and the more significant bond lengths and angles in Tables 3 and 4. Full data are deposited.\*

**Discussion.** These *MX<sub>2</sub>L<sub>2</sub>* compounds are all representative of the tetrahedral molecular series. Of the four compounds, (2) and (4) are isomorphous, and on the evidence from matching cell parameters, the Co bromide [CoBr<sub>2</sub>(Me<sub>3</sub>NO)<sub>2</sub>] also belongs to this same isomorphous group. The arrangement of these *C<sub>2</sub>* molecules in the crystal is shown in Fig. 1. They are seen to be aligned in rows with their diad axes parallel to the *y* axis of the cell, each row comprising molecules in a particular disposition. With the alternating axial (dipole) orientation of the molecules in successive bands parallel to (001), the halogen atoms fall into almost planar layers. The structure is at variance with the normal tendency for halogen

atoms (though not always for iodine) to be surrounded as fully as possible with C—H containing groups (see, for example, Robinson, Wilkins & Zhang, 1990); but the closest Br...Br approach (4.93 Å) in (4) and I...I (4.90 Å) in (2) remain well above the sum of the van der Waals radii.\* Nevertheless it is not surprising that the chlorides (1) and (3) develop alternative structures. For chlorides, higher polarity and shorter distances maximize C—H...Cl interactions. It is significant that with the *P2<sub>1</sub>* molecular packing shown by [ZnCl<sub>2</sub>(Me<sub>3</sub>NO)<sub>2</sub>] (3) (Fig. 2) the Cl atoms, while still falling into layers, are more completely surrounded by methyl groups and the minimum Cl...Cl approach is increased to 5.36 Å. The Cl atoms in each molecule of (3) have twelve Cl...C approach distances < 4.0 Å, while in (4) there are only nine Br...C approaches < 4.3 Å.

The asymmetric unit of (1) is unusual (Fig. 3). It comprises four structurally distinct molecules, although those centred on Co(1) and Co(4) have closely similar geometry. Differences over the four molecules arise primarily from variation in the Cl—Co—Cl and especially the O—Co—O bond angles (Table 3). The ease with which such angles can alter is well known and is understandable from

\* Lists of structure factors, anisotropic thermal parameters, bond distances and angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54629 (35 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

\* A molecular packing similar to that for (2) and (4) is developed by the dimethyl sulfoxide derivative [ZnI<sub>2</sub>(dmsO)<sub>2</sub>], which adopts the space group *P2<sub>1</sub>/n* (M. Nieuwenhuyzen, 1991; unpublished). Here there are two rows of molecules in reversed orientation passing through the cell. There are I...I distances falling to 4.449 and 4.513 Å.

the partial electrostatic nature of the  $M-O$  and  $M-Cl$  bonds (Robinson, Wilkins & Zhang, 1990). In the crystal there is preservation of the minimum  $Cl \cdots CH_3$  approach distances in the usual ranges,  $C \cdots Cl$  3.5–3.8 and  $H \cdots Cl$  2.9–3.2 Å. The two groups of carbon atoms C(1), C(2), C(3) and C(10), C(11), C(12), but not the respective N(11) and N(22) atoms which carry them, show high temperature factors. This must arise from a low rotational constraint on these C atoms, because they all show significantly fewer close intermolecular approaches (e.g.  $C \cdots Cl < 3.8$  Å) than do any of the other C atoms. Neither the electronic spectrum nor the vibrational spectrum of the crystalline compound bears evidence of the (limited) variations in molecular geometry.

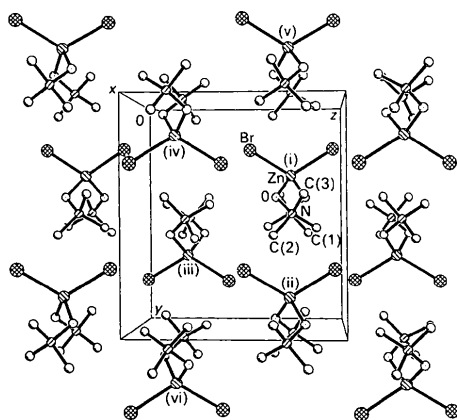


Fig. 1. The arrangement of molecules in  $[ZnBr_2(Me_3NO)_2]$  (4), as representative of the isomorphous group which also includes (2). H atoms are omitted. The layering of the halogen atoms parallel to (010) is evident. Symmetry codes for Zn atoms are: (i)  $x, y, z$ ; (ii)  $\frac{1}{2} - x, \frac{1}{2} + y, z$ ; (iii)  $x, 1 - y, z - \frac{1}{2}$ ; (iv)  $\frac{1}{2} - x, \frac{1}{2} - y, z - \frac{1}{2}$ ; (v)  $\frac{1}{2} - x, y - \frac{1}{2}, z$ ; (vi)  $\frac{1}{2} - x, \frac{1}{2} - y, z - \frac{1}{2}$ . This gives  $x$  coordinates for these Zn centres: 0.5 for (i) and (iii); 1.0 for (ii), (iv) and (vi).

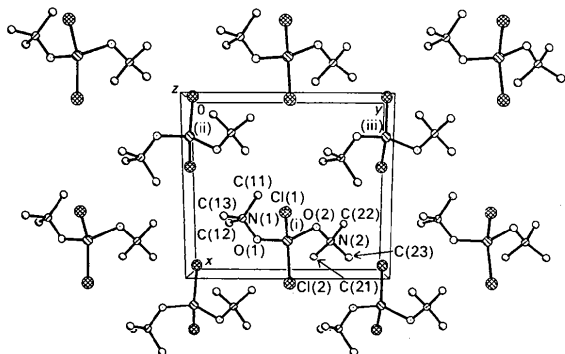


Fig. 2. The monoclinic cell of the  $[ZnCl_2(Me_3NO)_2]$  (3) crystal, viewed along the  $z$  axis. Symmetry codes for Zn atoms are: (i)  $x, y, z$ ; (ii)  $1 - x, y - \frac{1}{2}, 1 - z$ ; (iii)  $1 - x, y + \frac{1}{2}, 1 - z$ . In this molecule approximate  $C_2$  symmetry is retained overall.

Charge transfer in these molecules from the highly polar  $N-O$  bond to the metal centre calls for comment. Here, bond lengths in the Zn compounds  $ZnCl_2(Me_3NO)_2$  (3) and  $[ZnCl_2(py)_2]$  (McConnell, Day & Wood, 1986) offer comparison. From Table 4 it can be seen that for (3) the  $Zn-O$  bonds are shorter, but the  $Zn-Cl$  bonds are longer than for  $[ZnCl_2(py)_2]$ . This is consistent with a greater charge transfer (giving stronger bonding) from ligand to Zn in the  $Me_3NO$  compound. It is consistent with the higher  $N-O$  bond polarity in the amine oxide (Linton, 1940; Karayannis, Pytlewski & Mikulski, 1973), and also with the spectrochemical evidence that  $tmno$  is a better donor than  $pyo$  (Drago, Donoghue & Herlocker, 1965). Over all the molecules (1)–(4) the ligand  $N-O$  bond length is

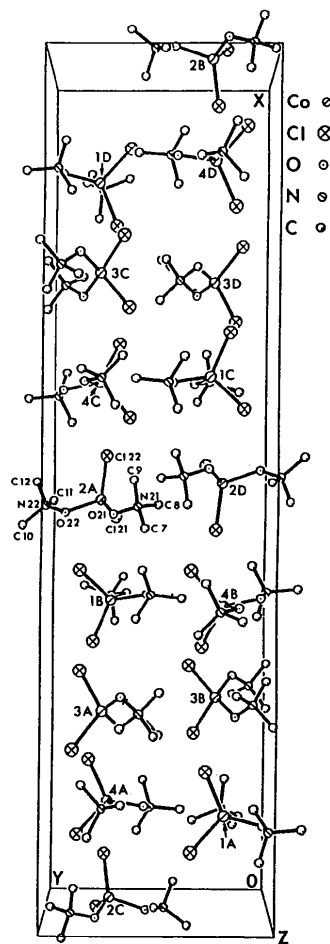


Fig. 3. The  $[CoCl_2(Me_3NO)_2]$  (1) cell, viewed along the  $z$  axis. The four independent Co atoms, Co(1), Co(2), Co(3), Co(4), are designated with  $A, B, C, D$  corresponding to the four (composite) asymmetric units contributing to the cell. Symmetry codes for the molecules shown are: Co(1A, 3A)  $x, y, 1 + z$ ; Co(2A, 4A)  $x, y, z$ ; Co(1B)  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$ ; Co(2B, 3B, 4B)  $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} + z$ ; Co(1C)  $\frac{1}{2} + x, \frac{1}{2} - y, 1 + z$ ; Co(2C, 4C)  $\frac{1}{2} + x, \frac{1}{2} - y, z$ ; Co(3C)  $\frac{1}{2} + x, \frac{3}{2} - y, 1 + z$ ; Co(1D, 2D, 3D, 4D)  $1 - x, 1 - y, \frac{1}{2} + z$ .

quite constant (1.414 Å average). This value is significantly greater than that for N—O in  $[\text{ZnCl}_2(\text{pyo})_2]$  (1.338 Å), showing that the pyo bond retains considerable  $\pi$  character even in the coordinated molecule.

The structural results eliminate the suggestion by Herlocker (1969) that differences between the electronic spectra of  $[\text{CoX}_2(\text{Me}_3\text{NO})_2]$  complexes run as mulls and in solution are a result of five coordination through ligand bridging in the crystals. Reinterpretation would suggest that, in solution, the polar solvent molecules (dichloromethane and acetonitrile) interact additionally with the metal centre to alter the field symmetry, but on crystallization these more weakly attracted solvent molecules are excluded. The earlier finding (Herlocker & Drago, 1968) that excess of the rather strongly bonding, but sterically demanding, amine oxide ligand displaces the spectral features towards those of  $[\text{Co}(\text{Me}_3\text{NO})_4](\text{ClO})_2$  (with ease of displacement  $\text{I} > \text{Br} > \text{Cl}$ ) is compatible with this view,

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### Structure of Dibutyltin Bis(*p*-nitrobenzoate)

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**Abstract.**  $[\text{Sn}(\text{C}_4\text{H}_9)_2(\text{C}_7\text{H}_4\text{NO}_4)_2]$ ,  $M_r = 565.15$ , monoclinic,  $C2/c$ ,  $a = 15.694$  (7),  $b = 7.042$  (5),  $c = 22.950$  (11) Å,  $\beta = 103.64$  (4)°,  $V = 2465$  (2) Å<sup>3</sup>,  $Z =$

4,  $D_x = 1.53$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 1.08$  mm<sup>-1</sup>,  $F(000) = 1144$ ,  $T = 293$  K,  $R = 0.054$  for 1023 observed reflexions. The compound is monomeric. The Sn atom lies on a crystallographic twofold axis and displays skew-trapezoidal bipyramidal coordination. The basal plane is defined by the two asymmetrically chelating carboxylate groups

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